



**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460**

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

MEMORANDUM

Date: 06/30/2014

SUBJECT: Pyraclostrobin: Petition for the Establishment of Permanent Tolerances and Registration for Use on Herb Subgroup 19A and Dill. Request for Crop Group Expansions/Revisions for Stone Fruit Group 12-12 and Tree Nut Group 14-12. Summary of Analytical Chemistry and Residue Data.

PC Code: 099100

Decision No.: 484923

Petition No.: 2E8216

Risk Assessment Type: Single Chemical/Aggregate

TXR No.: N/A

MRID Nos: 47014801, 47014802, 47014803

DP Barcode: D421145

Registration Nos.: 7969-185; 7969-199; 7969-258

Regulatory Action: Section 3 Registration

Case No.: N/A

CAS No.: 175013-18-0

40 CFR: 180.582

FROM: Stephen Funk, Senior Chemist
Risk Assessment Branch III (RAB III)
Health Effects Division (HED; 7509P)

THROUGH: Christine Olinger, Branch Chief
Risk Assessment Branch III (RAB III)
Health Effects Division (HED; 7509P)

TO: Barbara Madden, RM05
Andrew Ertman
Registration Division (RD; 7505P)

And

Barry O'Keefe, Senior Biologist
Risk Assessment Branch III (RAB III)
Health Effects Division (HED; 7509P)

OCSP 860 Series Guideline	MRID Number	Title
860.1500 Crop Field Trials	47014801	D. Carpenter, 2006, BAS 516: <i>Magnitude of the Residue in Dill</i> . Unpublished Study Prepared by BASF Agro Research, University of Florida and Artichoke Research Assn., Project No. 08691/03/BAR03, 08691, 2000/5001019. 214 p.
860.1500 Crop Field Trials	47014802	D. Carpenter, 2006, BAS 516: <i>Magnitude of the Residue on Chives</i> . Unpublished Study Prepared by BASF Agro Research, University of Maryland and U.S. Dept of Agriculture Agr. Res. Service, Project Number 08793, 08793/03/BAR05. 173 p.
860.1500 Crop Field Trials	47014803	D. Carpenter, 2006. BAS 5a6: <i>Magnitude of the Residue on Basil</i> . Unpublished Study Prepared by BASF Agro Research, Cornell University and Artichoke Research Assn, Project Number 08792, 08792/03/BAR04. 203 p.

Table of Contents

1.0	Executive Summary	4
2.0	Regulatory Recommendations.....	5
2.1	Data Deficiencies/Data Needs.....	5
2.2	Tolerance Considerations.....	5
2.2.1	Enforcement Analytical Method	5
2.2.2	Recommended Tolerances.....	6
2.2.3	Revisions to Petitioned-For Tolerances	6
2.2.4	International Harmonization.....	6
2.3	Label Recommendations.....	7
3.0	Introduction.....	7
3.1	Chemical Identity	7
3.2	Physical/Chemical Characteristics	8
3.3	Pesticide Use Pattern/Directions for Use (860.1200).....	8
4.0	Metabolite/Degradate Residue Profile.....	9
4.1	Nature of the Residue.....	9
4.1.1	Summary of Plant Metabolism (860.1300)	9
4.1.2	Summary of Livestock Metabolism (860.1300).....	9
4.1.3	Summary of Confined Rotational Crops (860.1850)	10
4.1.4	Summary of Metabolites and Degradates.....	10
4.2	Comparison of Metabolic Pathways.....	10
4.3	Residues of Concern Summary and Rationale.....	11
5.0	Residue Profile	11

5.1	Residue Analytical Methods (860.1340)	11
5.1.1	Data Collection Methods	11
5.1.2	Multi-Residue Methods (860.1360)	12
5.1.3	Tolerance Enforcement Methods	12
5.1.4	Submittal of Analytical Reference Standards (860.1650)	13
5.2	Storage Stability (860.1380)	13
5.3	Residue Data	13
5.3.1	Crop Field Trials (860.1500)	13
5.3.2	Field Rotational Crops (860.1900)	15
5.3.3	Processed Food and Feed (860.1520)	15
5.3.4	Meat, Milk, Poultry, and Eggs (860.1480)	16
5.3.5	Food Handling (860.1460)	16
5.3.6	Water, Fish, and Irrigated Crops (860.1400)	17
6.0	Tolerance Derivation	17
7.0	References	17
APPENDIX A: International Residue Limits		20
APPENDIX B: Tabular Summary of Metabolites		21
APPENDIX C: Determination of Tolerances for Pyraclostrobin in/on Dill Seed and Fresh Herbs		27

1.0 Executive Summary

Pyraclostrobin, or methyl *N*-[2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl] phenyl]-*N*-methoxycarbamate belongs to the strobilurin class of fungicides. The fungicide is currently registered to BASF Corporation (BASF) for use on a variety of field, vegetable, fruit, and nut crops. It is formulated as water-dispersible granules (WDG) or an emulsifiable concentrate (EC) and is typically applied as foliar applications using ground or aerial equipment at maximum seasonal rates of 0.3-3.0 lb ai/A. The 20% WDG formulation is also registered for use as a seed treatment on some crops.

The Interregional Research Project Number 4 (IR-4) is proposing new uses for pyraclostrobin on the herb subgroup 19A and dill. The relevant field trial data were reviewed previously, and that review is incorporated by reference: D343754, J. Stokes, B. Cropp-Kohlligan, and G. Otake, 02/12/2008. The proposed use for the herb subgroup 19A and for dill is up to two applications of a WG formulation with a seasonal maximum rate of 0.30 lb ai/acre and a 0-day PHI.

IR-4 is also requesting crop group conversions for stone fruit 12-12 and nut tree group 14-12.

Adequate metabolism studies with pyraclostrobin on grapes, potatoes, and wheat have been reviewed (D269668, 11/28/01, L. Cheng) in conjunction with PP#0F06139. The nature of the residue in livestock is adequately understood based on acceptable ruminant and poultry metabolism studies. HED (D278044, Metabolism Assessment Review Committee (MARC), 10/09/01) has determined that for purposes of tolerance and dietary risk assessments, the residues of concern in plant and rotational crop commodities include pyraclostrobin and its desmethoxy metabolite (BF 500-3). The residues of concern in livestock commodities include pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1*H*-pyrazol-3-ol (BF 500-5) and 1-(4-chloro-2-hydroxyphenyl)-1*H*-pyrazol-3-ol (BF 500-8).

There are adequate residue analytical methods for tolerance enforcement. The analytical methods for plant commodities are liquid chromatography with tandem mass spectrometry (LC/MS/MS) and high pressure liquid chromatography with ultraviolet detector (HPLC/UV), which both measure pyraclostrobin and its desmethoxy metabolite. The analytical methods for livestock commodities, gas chromatography with mass spectrometry (GC/MS) and LC/MS/MS, convert pyraclostrobin and related metabolites to chlorophenylpyrazolol (BF 500-5) and hydroxylated chlorophenylpyrazolol (BF 500-8) in goats and chlorophenylpyrazolol (BF 500-5) and a hydroxylated chlorophenylpyrazolol isomer of BF 500-8 (BF 500-9) in poultry.

IR-4 has submitted field trial data for four trials each for pyraclostrobin in basil (fresh and dried), in chives, and in dill (fresh and seed) in the USA. The test formulation used in all trials was BAS 500 02F, which was identified as either Headline® Fungicide (EPA Reg. No. 7969-186, 2.0 lbs ai/gal EC) or Cabrio® Fungicide (EPA Reg. No. 7969-187, 20% WDG). BAS 500 02F was applied as four directed foliar sprays at 0.19-0.21 lb ai/A/application for a total rate of 0.80-0.83 lb ai/A with a 0-day PHI. This application scenario does not match the proposed label.

Field trial samples (basil, dill, chives) were analyzed for pyraclostrobin and metabolite BF 500-3 using BASF Analytical Method Number D9908 (Version 2), "Method for Determining BAS 500 F, BF 500-3 and BAS 510 F Residues in Plant Matrices using LC/MS/MS." (MRID 4670001).

The method is adequate for data collection.

The requirements for multiresidue methods testing data are fulfilled. Pyraclostrobin was successfully evaluated through several of the FDA protocols (complete recovery through protocols D and E), while recovery of metabolite BF 500-3 was unsuccessful in all protocols.

Samples of dill, chive, and basil commodities were stored frozen for periods covered by existing storage stability data.

There are no feed commodities associated with chives, dill, or basil. Therefore, the livestock diets are not impacted, and the existing livestock commodity tolerances remain adequate.

Analytical reference standards for pyraclostrobin and its regulated metabolites are available at the EPA National Pesticide Standards Repository.

Adequate confined, limited and extensive field rotational crop studies are available supporting the existing tolerances for indirect residues of pyraclostrobin in rotational crops. These data support the 14-day plant-back interval currently specified for crops without pyraclostrobin uses. No additional rotational crop data are required for purposes of this petition.

2.0 Regulatory Recommendations

HED has examined the residue chemistry database for pyraclostrobin, and there are no residue chemistry deficiencies that would preclude granting Section 3 registration for the requested crop commodity uses of pyraclostrobin, or establishment of tolerances for residues of pyraclostrobin. The conversions of the stone fruit group 12-12 and tree nut group 14-2 are acceptable. The specific tolerance recommendations are discussed in section 2.2, and label modifications are discussed in section 2.3.

2.1 Data Deficiencies/Data Needs

There are no deficiencies or data needs related to the requested new registrations, new tolerances, and crop group conversions.

2.2 Tolerance Considerations

2.2.1 Enforcement Analytical Method

Two adequate methods are available for enforcement purposes for residues of pyraclostrobin and the metabolite BF 500-3 in/on plant commodities: an LC/MS/MS method (BASF Method D9908) and an HPLC/UV method (Method D9904). The validated method LOQ for both pyraclostrobin and BF 500-3 is 0.02 ppm in all tested plant matrices, for a combined LOQ of 0.04 ppm. Adequate independent method validation (MRID 45118501; MRID 45118503) and radiovalidation data were submitted for both methods.

Pyraclostrobin was successfully evaluated through several of the FDA protocols, while recovery of BF 500-3 was unsuccessful in all protocols. Pyraclostrobin was completely recovered through Protocol D (in grape) and E (in grape), and partially recovered through Protocol F (in peanut). Metabolite BF 500-3 had poor peak shape and inadequate sensitivity with Protocol C columns, and therefore, was not further analyzed under Protocol D, E, and F. The results of the multiresidue testing for pyraclostrobin were forwarded to FDA on 1/4/02 for the purpose of updating the *Pesticide Analytical Manual*, Volume I (PAM I).

2.2.2 Recommended Tolerances

It is recommended that tolerances be established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on dill seed and the herbs subgroup 19A. Compliance with the tolerance levels is to be determined by measuring only the sum of pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl *N*-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl carbamate), calculated as the stoichiometric equivalent of pyraclostrobin. The tolerance expression is aligned with the requirements of the S. Knizner 05/27/2009 memo.

Table 2.2.2. Tolerance Summary for Pyraclostrobin

Commodity	Proposed Tolerance (ppm)	Existing Tolerance	HED-Recommended Tolerance (ppm)	Comments (correct commodity definition)
Herb subgroup 19A	85	-	40	
Dill, seed	100	-	40	
Fruit, stone, group 12		2.5	Revoke	Crop group conversion
Fruit, stone, group 12-12	2.5	-	2.5	Crop group conversion
Nut, tree, group 14		0.04	Revoke	Crop group conversion
Nut, tree, group 14-12, except pistachio ¹	0.04	-	0.04	Crop group conversion

¹A separate tolerance exists for pistachio (0.7 ppm).

2.2.3 Revisions to Petitioned-For Tolerances

The proposed tolerance for the herb subgroup 19A and the proposed tolerance for dill seed are based on the use of field trial data without adjustment for the exaggerated application rate (2.7X) represented by those trials. Each of the two applications of pyraclostrobin were conducted at 2.7X the label rate, and the total seasonal rate was 2.7X the label rate. Using the assumption of proportionality, that is, that the residue levels are proportional to the rate of application, the residue results may be adjusted to the concentrations expected at the 1X rate. The tolerance estimates at the 1X rate are 40 ppm for herb subgroup 19A and 40 ppm for dill seed. A revised section F must be submitted.

2.2.4 International Harmonization

The Codex and US residue definitions for pyraclostrobin residues on plant commodities are different. The Codex definition is pyraclostrobin, whereas the US definition is pyraclostrobin and its desmethoxy metabolite. Codex has not established MRLs for pyraclostrobin on herbs or dill seed, and therefore there are no harmonization issues. Codex has established MRLs for

some members of the stone fruit group, i.e., cherries (3 mg/kg), peach/nectarine (0.3 mg/kg), and plums (0.8 ppm), but does not have a group tolerance. Codex has established a tree nut group tolerance at 0.02 mg/kg. The US tolerance cannot be lowered, as it includes parent and a metabolite, each at 0.02 ppm, or 0.04 ppm total.

The Canada and US definitions for the pyraclostrobin residue are harmonized. Canada has not established MRLs for herbs or dill seed. Canada has MRLs for tree nuts, and these are harmonized with the US. Canada has established MRLs for various stone fruits at 0.7 ppm. The US tolerance for stone fruits prior to 2009 was 0.9 ppm. However, the tolerance was increased to 2.5 ppm to accommodate European Union import requirements (D359194, M. Negussie, 04/01/2009; PP#8F7390).

Refer to Appendix A for the International Residue Limits status.

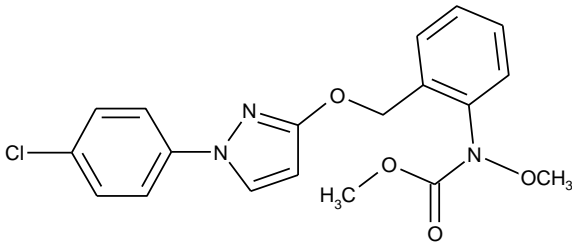
2.3 Label Recommendations

The proposed labels are acceptable.

3.0 Introduction

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination and mycelial growth and sporulation of the fungus on the leaf surface.

3.1 Chemical Identity

Table 3.1 Pyraclostrobin Nomenclature.	
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl 2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]-N-methoxycarbamate
CAS name	methyl N-[2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]-N-methoxycarbamate
CAS registry number	175013-18-0
End-use product (EP)	Pyraclostrobin Technical, EPA Reg. No. 7969-185 Pyraclostrobin Crystalline, EPA Reg. No. 7969-258 Pristine® Fungicide, EPA Reg. No. 7969-199

3.2 Physical/Chemical Characteristics

Table 3.2 Physicochemical Properties of Technical Grade Pyraclostrobin.		
Parameter	Value	References ¹ (MRID)
Melting point/range	63.7-65.2°C	45118213
pH	Not applicable	
Density	1.367 g/cm ³	45118214
Water solubility at 20 °C	1.9 ± 0.17 mg/L (deionized water, pH 5.8)	45118233
Solvent solubility	n-heptane (0.37 g/100mL); 2-propanol (3.0 g/100mL); 1-octanol (2.42 g/100mL); olive oil (2.80 g/100mL); methanol (10.08 g/100mL); >50 g/100mL in acetone, ethyl acetate, acetonitrile, dichloromethane and toluene.	45118228
Vapor pressure	2.6 x 10 ⁻¹⁰ hPa at 20 °C	45118214
Dissociation constant, pK _a	None (no dissociable moieties)	
Octanol/water partition coefficient, Log(K _{ow}) at room temperature	3.990 mean log Pow; Pow is 9772	45118215
UV/visible absorption spectrum	The structural identity of BAS 500 F was confirmed by NMR and MS spectra. UV molecular extinction (e [1 mol ⁻¹ cm ⁻¹]): 2.5x10 ⁴ at 205 nm; 2.4x10 ⁴ at 275 nm.	1996/10955 ²

¹ Product Chemistry data were reviewed by the Registration Division (DP# 269848 and DP# 274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

² BASF Document Number.

3.3 Pesticide Use Pattern/Directions for Use (860.1200)

Proposed supplemental labels were provided for end use product 7969-199 (Pristine® fungicide). The supplemental labels address the crop group conversion and the new uses on herbs and dill seed. Pristine® contains two active ingredients, pyraclostrobin and boscalid. Only pyraclostrobin is considered in this document; boscalid is being evaluated separately.

Table 3.3 Summary of Proposed Directions for New Use of Pyraclostrobin						
Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations
Herb Subgroup 12A and Dill						
Foliar, ground or aerial	12.8% Pristine® WG 7969-199	0.15	2	0.30	0	For aerial application, use no less than 5 gallons of spray solution per acre. Repeat applications at a minimum of 7 days. To limit development of resistance, do not make more than 2 applications per season. REI is 12 hours.

The proposed label for end use product #7969-199 (Pristine® fungicide) includes changes for crop group/subgroup conversions. The stone fruit group was expanded from the commodities of group 12 to the commodities of group 12-12. The tree nut group was expanded from the commodities of group 14 to the commodities of group 14-12. Although pistachio is a member of

group 14-12, it was excluded because a tolerance exists at a substantially higher value than the tree nut group tolerance. No changes were made in the good agricultural practices (GAPs) for stone fruits and tree nuts from the previous label of 06/04/2012.

Conclusions: The submitted use directions are sufficient to allow for evaluation of the submitted residue data relative to the proposed use pattern for herb subgroup 19A and dill. The proposed label changes related to crop group/subgroup conversions are acceptable. There are no label deficiencies.

4.0 Metabolite/Degradate Residue Profile

4.1 Nature of the Residue

4.1.1 Summary of Plant Metabolism (860.1300)

HED MARC, DP# 278044, L. Cheng, 10/9/01

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

Adequate metabolism studies with pyraclostrobin on grapes, potatoes, and wheat have been reviewed (D269668, 11/28/01, L. Cheng) in conjunction with PP#0F06139. The results of these studies indicate that the metabolism of pyraclostrobin is similar in the three crops investigated. The HED Metabolism Assessment Review Committee (MARC) discussed the results of these studies on 9/20/01, and concluded that the nature of the residue in plants is understood. For the purpose of tolerance and risk assessment, the terminal residues of concern in plants consist of pyraclostrobin and its desmethoxy metabolite (BF 500-3).

4.1.2 Summary of Livestock Metabolism (860.1300)

HED MARC, DP# 278044, L. Cheng, 10/9/01

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

The nature of the residue in livestock is adequately understood based on acceptable ruminant and poultry metabolism studies. In *goat*, the major residues are pyraclostrobin and BF 500-3 in muscle and fat; pyraclostrobin, BF 500-3, and BF 500-5 and its sulfate conjugate in milk; pyraclostrobin, BF 500-3, and BF 500-5 and its sulfate conjugate, and hydroxylated desmethoxy metabolite (500M67) in kidney; and metabolites hydrolyzed to BF 500-5 and its hydroxylated compound (BF 500-8) in liver. In *poultry*, the major residues are pyraclostrobin and BF 500-3 in eggs; pyraclostrobin, BF 500-3, and hydroxylated BF 500-3 (500M64) in fat; and the glucuronic acid conjugate of hydroxylated BF 500-3 (500M32) in liver. Radioactive residues were below detection in muscle. The main degradation reactions in livestock consist of demethoxylation, hydroxylation, and conjugation, and breaking of the ether bond.

HED has determined that for the tolerance and risk assessment, the residues of concern in livestock commodities consist of pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1*H*-pyrazol-3-ol (BF 500-5) and 1-(4-chloro-2-hydroxyphenyl)-1*H*-pyrazol-3-ol (BF 500-8).

4.1.3 Summary of Confined Rotational Crops (860.1850)

MARC, DP# 278044, L. Cheng, 10/9/01

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

An adequate confined rotational crop study was reviewed in PP#0F6139. The study showed that the metabolism of pyraclostrobin in rotated crops is similar but more extensive than that in primary crops. Pyraclostrobin undergoes demethoxylation to yield BF 500-3, followed by further degradation to polar metabolites, and subsequent conjugation reactions and incorporation into natural products. The HED MARC has determined that the residues of concern in rotational crops consist of pyraclostrobin and metabolite BF 500-3.

4.1.4 Summary of Metabolites and Degradates

Appendix B provides a list of metabolites and degradates and the associated matrices of the metabolism studies.

4.2 Comparison of Metabolic Pathways

Pyraclostrobin and its desmethoxy metabolite (BF500-3) are the major residues in most crop matrices including livestock feeds; tryptophan was found to be the major residue in potato tuber and wheat grain when carbon-14 was introduced in the tolyl ring (*via* the shikimic acid pathway). The major degradation reactions are the removal of the methoxy group from the carbamate nitrogen and breakage of the ether bond.

Results of the confined rotational crop studies show that pyraclostrobin and its desmethoxy metabolite are the major residues taken up into the plants.

In goats, the major residues are pyraclostrobin and BF500-3 in muscle and fat; parent, BF500-3, and BF500-5 and its sulfate conjugate in milk; parent, BF500-3, and BF500-5 and its sulfate conjugate, and hydroxylated desmethoxy metabolite (500M67) in kidney; and metabolites hydrolyzed to BF500-5 and its hydroxylated compound (BF500-8) in liver.

In poultry, the major residues are pyraclostrobin and BF500-3 in eggs; parent, BF500-3, and hydroxylated BF500-3 (500M64) in fat; and the glucuronic acid conjugate of hydroxylated BF500-3 (500M32) in liver. Radioactive residues were below quantitation in muscle.

The main degradation reactions in livestock consist of demethoxylation, hydroxylation, and conjugation, and breaking of the ether bond.

For the rat, the bulk of pyraclostrobin is excreted *via* the urine (11-16%) and feces (85%). A large number of metabolites (nearly 33) were isolated and identified in the urine, feces, and bile. These metabolites indicate that demethoxylation, hydroxylation and cleavage of the ether bond are the major metabolic reactions in rats, similar pathways to ruminant and poultry.

4.3 Residues of Concern Summary and Rationale

MARC Memo, 10/09/2001, D278044

Table 4.3. Summary of Metabolites and Degradates to be included in the Risk Assessment and Tolerance Expression			
Matrix		Residues included in Risk Assessment	Residues included in Tolerance Expression
Plants	Primary Crop	Pyraclostrobin + Desmethoxy Metabolite BF500-3	Pyraclostrobin + Desmethoxy Metabolite BF500-3
	Rotational Crop	Pyraclostrobin + Desmethoxy Metabolite BF500-3	Pyraclostrobin + Desmethoxy Metabolite BF500-3
Livestock	Ruminant	Pyraclostrobin + Metabolites convertible to BF500-5 and BF500-8	Pyraclostrobin + Metabolites convertible to BF500-5 and BF500-8
	Poultry	Pyraclostrobin + Metabolites convertible to BF500-5 and BF500-8	Pyraclostrobin + Metabolites convertible to BF500-5 and BF500-8
Drinking Water		Pyraclostrobin	Not Applicable

5.0 Residue Profile

5.1 Residue Analytical Methods (860.1340)

5.1.1 Data Collection Methods

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

PP#0F6139, DP# 269850, L. Cheng, 11/8/00

Samples from field trial studies were analyzed for pyraclostrobin and its metabolite BF 500-3 using BASF Analytical Method Number D9908, "Method for Determining BAS 500 F, BF 500-3 and BAS 510 F Residues in Plant Matrices using LC/MS/MS." This method is similar to the enforcement method. Briefly, residues of pyraclostrobin and BF 500-3 were extracted from the commodity samples with a 70:25:5 methanol/water/2 N HCl mixture. An aliquot of the extract was removed and cleaned by liquid/liquid partition with cyclohexane and 1N HCl saturated with NaCl. An aliquot of the cyclohexane phase was taken, evaporated to dryness, and re-dissolved in a buffered methanol:water solution (80:20, v:v, each containing 0.1% formic acid and 4 mM ammonium formate) for analysis by LC/MS/MS. The final chromatographic analysis of residues was determined by MS/MS detection using the positive ionization mode and monitoring ion transitions from m/z 388→194 for pyraclostrobin and m/z 358→164 for BF 500-3. Total residues of pyraclostrobin and BF 500-3 are expressed as pyraclostrobin equivalents.

The LLMV in the studies was 0.02 ppm for each of pyraclostrobin and BF 500-3 on the dill and chive commodities, but 0.05 ppm for each of pyraclostrobin and BF 500-3 on the basil commodities. Concurrent recovery experiments were conducted on fresh basil at fortification levels of 0.05 ppm, 5 ppm, and 50 ppm for each of pyraclostrobin and its metabolite BF-500-3 and on dry basil at fortification levels of 0.05 ppm, 50 ppm, and 200 ppm for each analyte. Recoveries were in the range of 74% to 119%. Concurrent recoveries from fortifications of fresh dill and dill seed with each of pyraclostrobin and BF-500-3 at fortifications of 0.02 ppm, 5.0

ppm, and 40.0 ppm (fresh dill) or 0.02 ppm, 5.0 ppm, and 200 ppm (dill seed) ranged from 71 – 109% for pyraclostrobin and from 67 – 115% for BF-500-3. Only one recovery was below 70%. Concurrent recoveries from fortifications of fresh chive samples with each of pyraclostrobin and BF-500-3 at fortifications of 0.02 ppm, 5 ppm, and 50 ppm ranged from 72% to 115%.

Conclusions: There are adequate residue analytical methods for data collection. The method was validated by concurrent recovery determinations in the subject crop field trials.

5.1.2 Multi-Residue Methods (860.1360)

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

Pyraclostrobin was successfully evaluated through several of the FDA protocols, while recovery of BF 500-3 was unsuccessful in all protocols. Pyraclostrobin was completely recovered through Protocol D (in grape) and E (in grape), and partially recovered through Protocol F (in peanut). Metabolite BF 500-3 had poor peak shape and inadequate sensitivity with Protocol C columns, and therefore, was not further analyzed under Protocol D, E, and F. The results of the multiresidue testing for pyraclostrobin were forwarded to FDA on 1/4/02 for the purpose of updating the *Pesticide Analytical Manual*, Volume I (PAM I).

5.1.3 Tolerance Enforcement Methods

PP#0F6139, D# 269668, L. Cheng, 11/28/01

PP#0F6139, D# 269850, L. Cheng, 11/8/00

PP#7E7245, D#381720, J. J. Stokes, 02/12/08

Two adequate methods are available for enforcement purposes for residues of pyraclostrobin and the metabolite BF 500-3 in/on plant commodities: an LC/MS/MS method (BASF Method D9908) and an HPLC/UV method (Method D9904). The validated method LOQ for both pyraclostrobin and BF 500-3 is 0.02 ppm in all tested plant matrices, for a combined LOQ of 0.04 ppm. Adequate independent method validation and radiovalidation data were provided for both methods. The LC/MS/MS is quite similar to the data collection method.

In PP#0F6139, two tolerance enforcement methods were proposed for ruminant commodities: HPLC/UV Method 439/0 and Method 446, consisting of GC/MS method 446/0 and LC/MS/MS method 446/1. The HPLC/UV method determines residues of pyraclostrobin *per se*. Method 446 has a hydrolysis step, and determines residues of pyraclostrobin and its metabolites as BF 500-5 and BF 500-8. The validated method LOQs for BF 500-5 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues, and the validated LOQs for BF 500-8 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues. Independent method validation data for the HPLC/UV and LC/MS/MS methods are acceptable. Radiovalidation data submitted for the GC/MS and LC/MS/MS methods are adequate for liver and milk, and marginal for muscle. An enforcement method for poultry was reviewed in PP#0F06139. However, tolerances for poultry egg and tissues have not been established and are not required for the purpose of the current petition.

5.1.4 Submittal of Analytical Reference Standards (860.1650)

Analytical standards for pyraclostrobin and regulated metabolites (BF 500-3; BF 500-5; BF 500-8) are currently available in the EPA National Pesticide Standards Repository (e-mail correspondence with T. Cole, 01/14/2013).

5.2 Storage Stability (860.1380)

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

Fresh dill samples were stored frozen ($<-10^{\circ}\text{C}$) from collection to extraction and analysis for a maximum of 171 days (5.7 mo), and dill seed samples were stored frozen ($<-10^{\circ}\text{C}$) from collection to extraction and analysis for a maximum of 147 days (4.9 mo). Fresh basil samples were stored frozen ($<-10^{\circ}\text{C}$) from collection to extraction and analysis for a maximum of 172 days (5.7 mo), and dried basil samples were stored frozen ($<-10^{\circ}\text{C}$) for a maximum of 161 days (5.4 mo). Fresh chive samples were stored frozen ($<-10^{\circ}\text{C}$) from collection to extraction and analysis for a maximum of 115 days (3.8 mo). Adequate storage stability data are available demonstrating that residues of pyraclostrobin and its metabolite BF 500-3 are stable under frozen conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. It was concluded that the plant commodities chosen for the storage stability study were representative of all crops: an oilseed (peanut nutmeat), a non-oily grain (wheat grain), a leafy vegetable (sugar beet tops), a root crop (sugar beet roots), a fruit/fruiting vegetable (tomatoes), a dry feed (wheat straw), and processed oil (peanut) and juice (grape) commodities (DP#s 269668 *etc.*, L. Cheng, 11/28/01). These data are adequate to support the storage conditions and durations of samples from the submitted field trials.

Conclusions: These data are adequate to support the storage conditions and durations of samples from the dill, chives, and basil crop field trials. No correction to residue values for loss during storage is necessary.

5.3 Residue Data

5.3.1 Crop Field Trials (860.1500)

D381720, J. Stokes, 02/12/2008

47014801.der (chives)

47014802.der (basil)

47014803.der (dill)

Basil

IR-4 has submitted field trial data for pyraclostrobin on basil. Four field trials were conducted in NAFTA Growing Zones 1 (NY, 1 trial), 3 (FL, 1 trial), 10 (CA, 1 trial), and 11 (WA, 1 trial) during the 2003 growing season. The test formulation used in all trials was BAS 500 02F, which was identified as either Headline® Fungicide (EPA Reg. No. 7969-186, 2.0 lb/gal EC) or Cabrio® Fungicide (EPA Reg. No. 7969-187, 20% WDG). BAS 500 02F was applied to basil as four directed foliar sprays at 0.20-0.21 lb ai/A/application for a total rate of 0.80-0.83 lb ai/A (2.7x the maximum proposed seasonal rate of 0.3 lb ai/A). Applications were made beginning when basil plants were at the vegetative/flowering stage and repeated one time on a 6- to 8-day retreatment interval using ground equipment (28-54 gal/A of spray volume) and did not include

the use of a spray adjuvant. Single control and duplicate treated samples of fresh basil were harvested from each test site at 0 and 3 days after treatment (DAT). Additional fresh basil samples were collected at 0 DAT and then dried according to simulated commercial practices in order to generate residue data for dried basil.

One trial was conducted in each of growing zones 1, 3, 10, and 11. The guideline request is for 3 trials minimum with no geographic distribution specified.

Chive

In a total of four field trials conducted during 2003, pyraclostrobin (BAS 500 02F) was applied to chives as four broadcast foliar sprays at 0.20-0.21 lb ai/A/application through vegetative development at RTIs of 6-8 days, for totals of 0.81-0.83 lb ai/A. All applications were made using ground equipment at 24-50 gal/A, and did not include the use of a spray adjuvant. Single control and duplicate treated samples of chives were harvested from each test at 0 DAT.

One trial was conducted in each of growing zones 2, 5, 10, and 11. The guideline request is for 3 trials minimum with no geographic distribution specified.

Dill

In a total of four field trials conducted during 2003, pyraclostrobin was applied to dill as four directed foliar applications at 0.19-0.21 lb ai/A/application from vegetative development stage through seed production with RTIs of 6-8 days, for totals of 0.80-0.83 lb ai/A. All applications were made using ground equipment at 28-62 gal/A, and did not include the use of a spray adjuvant. At the FL trial, a fifth application was made to the plot designated for seed harvest, as the crop was immature at the time of the fourth application. A total of 1.0 lb ai/A was applied to this FL plot. Single control and duplicate treated samples of fresh dill and dill seed were harvested from each trial site at 0 DAT.

One trial was conducted in each of growing zones 2, 3, 10, and 11. The guideline request is for 3 trials minimum with no geographic distribution specified.

Combined residues from the FL trial that included a fifth application to dill seed were 49.2 and 54.4 ppm, an apparent outlier. These values were not included in the statistical calculation.

Crop field trial summary residue data are presented in Table 5.3.1

Table 5.3.1. Summary of Residue Data from Field Trials with Pyraclostrobin.

Crop Matrix	Total Applic. Rate (lb ai/A)	PHI (days)	Combined Residue Levels of Pyraclostrobin and its Metabolite BF 500-3 (ppm)						
			n	Min.	Max.	HAFT	Median (STMdR)	Mean (STMR)	Std. Dev.
BASIL. Proposed use pattern: Two foliar sprays at 0.15 lb ai/A/application for a seasonal rate of 0.3 lb ai/A with a 0-day PHI.									
Fresh Basil	0.80-0.83	0	8	7.2	21.1	16.1	8.9	10.9	4.5
		3-4	8	1.3	7.5	7.4	4.9	4.8	2.6
Dried Basil		0	4	40.1	80.6	80.6	74.7	67.5	18.5
CHIVES. Proposed use pattern: Two foliar sprays at 0.15 lb ai/A/application for a seasonal rate of 0.3 lb ai/A with a 0-day PHI.									
Chives	0.81-0.83	0	8	0.7	8.8	7.8	6.9	5.8	3.1
DILL. Proposed use pattern: Two foliar sprays at 0.15 lb ai/A/application for a seasonal rate of 0.3 lb ai/A with a 0-day PHI.									
Dill weed	0.81-0.82	0	8	3.98	19.54	19.01	9.66	10.46	5.79
Dill Seed	0.80-0.83	0	6	3.60	22.60	21.20	18.30	14.45	8.34

Conclusions:

All studies were conducted at a seasonal rate of 0.80 lb ai/acre (2X0.40 lb ai/acre) with a 0-day PHI. The proposed use pattern (GAP) is 0.30 lb ai/acre (2X0.15 lb ai/acre) with a 0-day PHI. The trials were at a 2.7X exaggerated rate, for each application and for the seasonal application. Proportionality will be used to adjust the experimental data to the 1X rate.

The number and geographic distribution of the trials are adequate. The analytical method was demonstrated to be acceptable via concurrent recoveries of fortified control samples. The intervals of frozen storage of samples are covered by previous storage stability studies, and no corrections for loss of residue are needed. The results of the field trials are acceptable for estimation of tolerances and for dietary risk assessment purposes.

5.3.2 Field Rotational Crops (860.1900)

PP#0F6139, DP# 269668, L. Cheng, 11/28/01

A limited field rotational crop study was reviewed in PP#0F6139. The results indicate that residues of pyraclostrobin and its metabolite BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on rotational crop matrices (radish, roots and tops; cabbage, with and without wrapper leaves; and wheat forage, hay, and grain) planted 14 days following the last of six sequential foliar applications to the primary crop, cucumbers, of the 2 lb/gal EC formulation at 0.19 - 0.20 lb ai/A/application. Residues of pyraclostrobin in/on one sample of wheat straw from the CA test site were at the LOQ (0.02 ppm), but residues of pyraclostrobin in/on a replicate sample from the same plot were below the LOQ (0.012 ppm) for an average residue of <0.02 ppm. Residues of metabolite BF 500-3 were nondetectable (<0.02 ppm) in/on all samples of wheat straw.

The registered pyraclostrobin end-use product labels presently specify a 14-day plantback interval restriction for all crops that are not registered.

5.3.3 Processed Food and Feed (860.1520)

47014802 (basil)

Basil from each of the four field trials was dried.

Table 5.3.3. Residue Data from the Basil Processing Study with Pyraclostrobin

RAC (trial #)	Processed Commodity	Total Rate lb ai/A	PHI (day)	Residues (ppm)			Processing Factor		
				Pyraclo- strobin	BF 500-3	Combined	Pyraclo- strobin	BF 500-3	Combined
Fresh Basil (NY17)	RAC (prior to processing)	0.83	0	7.77	0.091	7.86	-	-	-
	Dried Basil			39.72	0.385	40.1	5.1	4.2	5.1
Fresh Basil (FL55)	RAC (prior to processing)	0.82	0	10.8	0.225	11.1			
	Dried Basil			78.8	1.77	80.6	7.3	7.9	7.3
Fresh Basil (CA125)	RAC (prior to processing)	0.80	0	15.8	0.234	16.1			
	Dried Basil			72.7	1.07	73.8	4.6	4.6	4.6
Fresh Basil (WA18)	RAC (prior to processing)	0.82	0	8.24	0.146	8.39			
	Dried Basil			74.4	1.34	75.7	9.0	9.2	9.0

The median processing factor (combined residues of pyraclostrobin and BF 500-3) is 6.2X.

Conclusion:

The four processing studies conducted for the production of dried basil are adequate to estimate a processing factor for the combined residue of pyraclostrobin and BF 500-3. In each of the trials, the fresh basil contained quantifiable residues of parent and metabolite.

5.3.4 Meat, Milk, Poultry, and Eggs (860.1480)

PP#1F6313; DP# 278385, M. Nelson, 8/15/2003

DP# 322235; D. Dotson, 11/03/2005

45405110.der (cattle feeding study)

45643801.der (poultry feeding study)

47584403.der (cattle feeding study)

DP# 364447; A. Acierto, 10/16/2009

There are no feed items associated with the requested new uses (basil, chives, dill). Therefore, no new considerations are required for residues in meat, milk, poultry, and eggs.

5.3.5 Food Handling (860.1460)

This guideline requirement is not relevant to the current petition as there are no food-handling uses being proposed for pyraclostrobin.

5.3.6 Water, Fish, and Irrigated Crops (860.1400)

This guideline requirement is not relevant to the current petition as there are no aquatic uses being proposed for pyraclostrobin.

6.0 Tolerance Derivation

The Organization for Economic Cooperation and Development (OECD) calculation procedure was used to determine tolerance estimates for the relevant commodities. Residue values were adjusted to the proposed 1X application rate by use of a 0.38 factor ($0.30 / 0.80$). See Appendix C.

The tolerance estimates for the fresh herbs, i.e., fresh basil, fresh dill weed, and fresh chives are 15 ppm, 15 ppm, and 8 ppm, respectively. The tolerance estimate for dried basil is 40 ppm (6.11 ppm HAFT X 6.2 processing factor = 37.9 ppm). The recommended tolerance for the herbs subgroup 19A, which encompasses both fresh and dried herbs, is 40 ppm.

The tolerance estimate for dill seed, a spice, is 40 ppm.

7.0 References

DP#s: 367409
Subject: Pyraclostrobin. Petition for New Uses and Tolerances on Alfalfa. Summary of Analytical Chemistry and Residue Data.
From: W. Cutchin
To: T. Kish/J. Bazuin
Dated: 10/19/09
MRIDs: 47584401

DP#s: 281042, 286732, 287729, 288459, 290342, 290343, 290369, 292440, 293088, 293684, 295893, 298178
Subject: Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and 2F06139. Petitions for the establishment of permanent tolerances to allow uses on corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, *Brassica* leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical Chemistry and Residue Data.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 7/26/04
MRIDs: 45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802, 45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802, 45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102

DP#s: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429
Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data.

From: L. Cheng

To: C. Giles-Parker/J. Bazuin

Dated: 11/28/01

MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

DP#: 278044

Subject: PP# 0F06139. PC Code 099100. Pyraclostrobin. Outcome of the HED Metabolism Assessment Review Committee (MARC) Meeting Held on September 20, 2001.

From: L. Cheng

To: Y. Donovan

Dated: 10/09/01

MRIDs: None

DP#: 269850

Subject: PP# 0F06139. Pyraclostrobin (BAS 500F) in or on Various Crops. Request for Tolerance Method Validation (TMV) Trial.

From: L. Cheng

To: F. D. Griffith, Jr.

Dated: 11/8/00

MRIDs: 45118505, 45118504, 45118509, 45118510, 45118501, 45118503, 45118507, 45118514

DP#: 281042, 286732, 287729, 288459, 290342, 290343, 290369, 292440, 293088, 293684, 295893, 298178

Subject: Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and 2F06139. Petitions for the establishment of permanent tolerances to allow uses on corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, *Brassica* leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical Chemistry and Residue Data.

From: L. Cheng

To: Cynthia Giles-Parker

Dated: 7/26/04

MRIDs: 45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802, 45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802, 45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102

APPENDIX A: International Residue Limits**Pyraclostrobin (099100; 02/19/2013)**

Summary of US and International Tolerances and Maximum Residue Limits				
Residue Definition:				
US	Canada	Mexico ²	Codex ³	
40 CFR §180.582. Plants: Tolerances are established for residues of the fungicide pyraclostrobin, including its metabolites and degradates. Compliance with the tolerance levels is to be determined by measuring on the sum of pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H- pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl N-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl carbamate), calculated as the stoichiometric equivalent of pyraclostrobin	methyl [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]met hoxycarbamate, including the metabolite [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]car bamate	-	Pyraclostrobin. Residue is NOT fat soluble.	
Commodity ¹	Tolerance (ppm) /Maximum Residue Limit (ppm)			
	US	Canada	Mexico ²	Codex ³
Herbs, subgroup 19A (fresh and dried)	40	None		None
Dill seed	40	None		None
Tree nuts	0.04	0.04		0.02 (*)
Stone fruit	2.5	0.7 (apricot, nectarine, peach, plumcot, plum cherries)		Cherries 3; Peach/nectarine 0.3; Plum 0.8

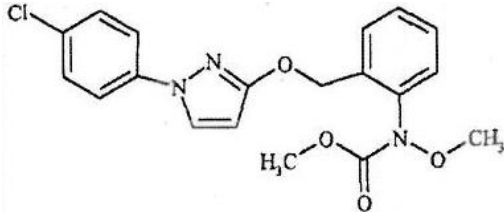
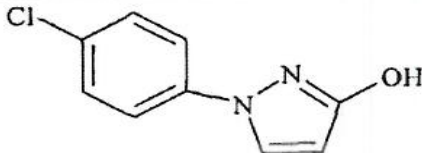
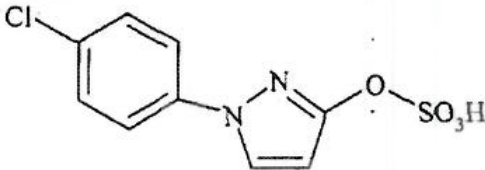
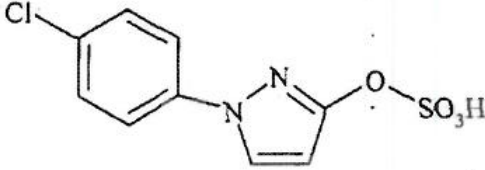
¹ Includes only commodities of interest for this action. Tolerance values should be the HED recommendations and not those proposed by the applicant.

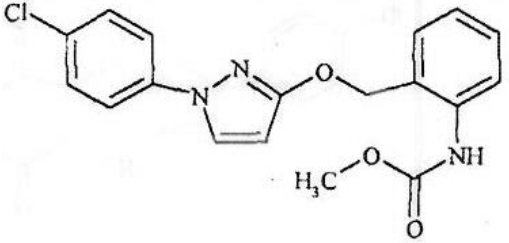
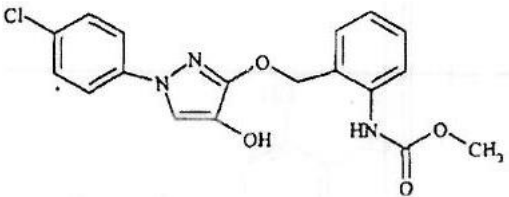
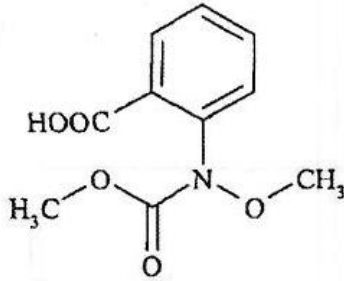
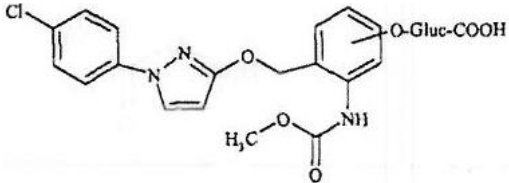
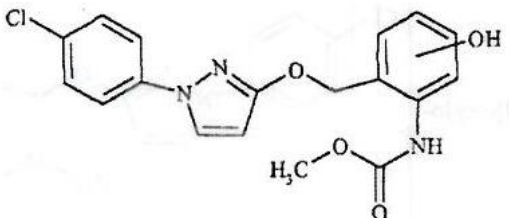
² Mexico adopts US tolerances and/or Codex MRLs for its export purposes.

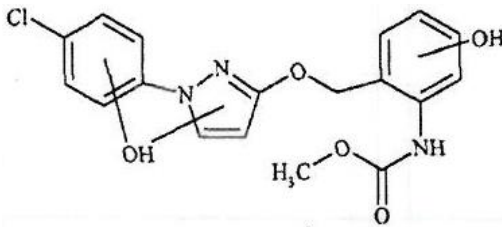
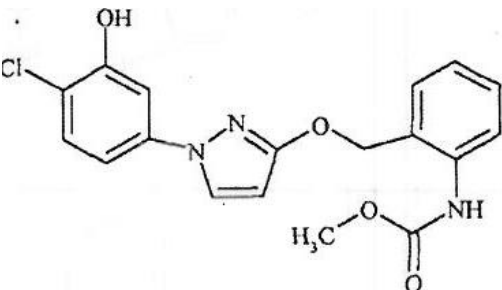
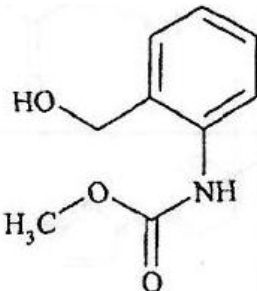
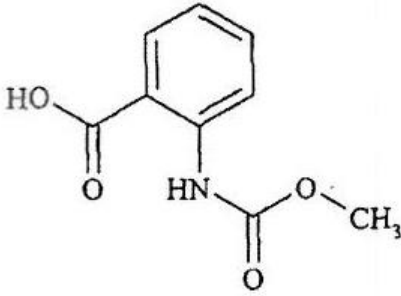
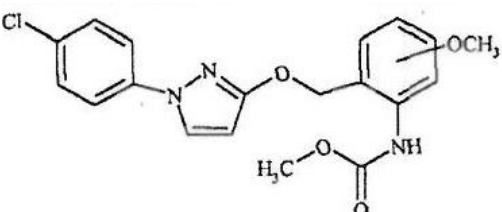
³ * = absent at the limit of quantitation; Po = postharvest treatment, such as treatment of stored grains. PoP = processed postharvest treated commodity, such as processing of treated stored wheat. (fat) = to be measured on the fat portion of the sample. MRLs indicated as proposed have not been finalized by the CCPR and the CAC.

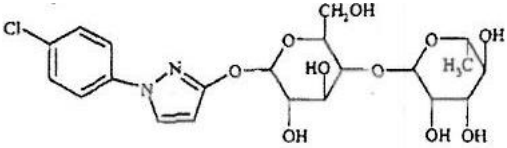
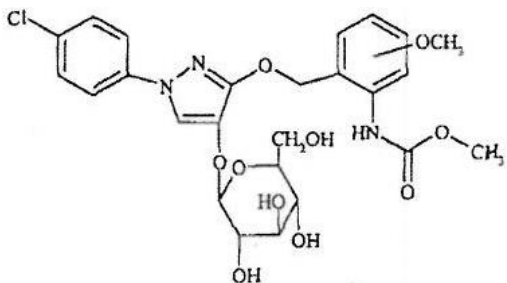
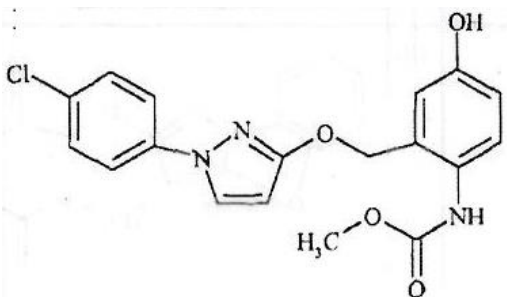
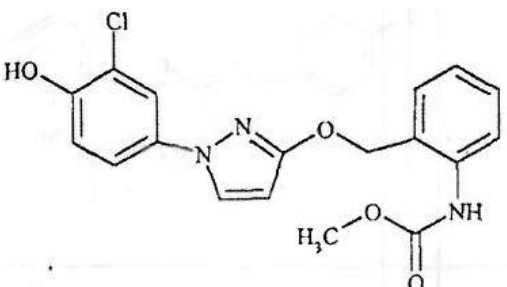
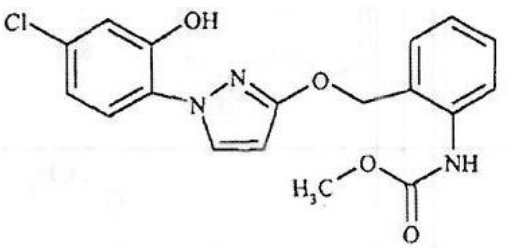
APPENDIX B: Tabular Summary of Metabolites

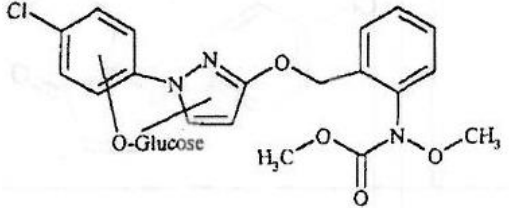
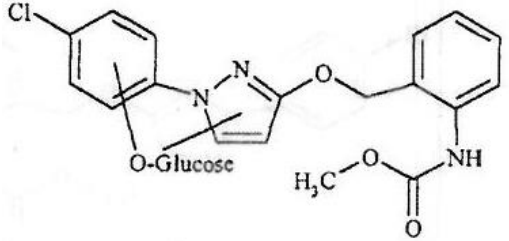
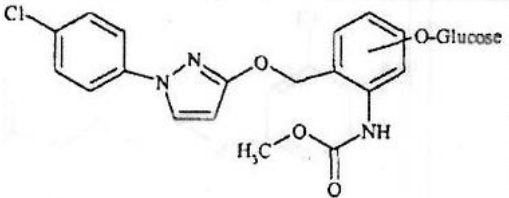
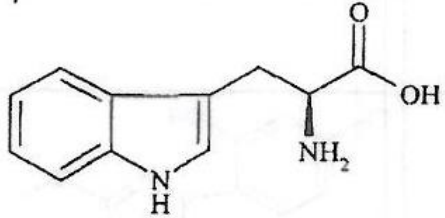
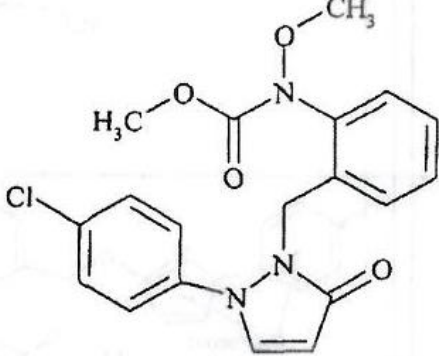
Figure B.1. Chemical names and structures of pyraclostrobin and its metabolites in plant, animal, and rotational crop commodities.

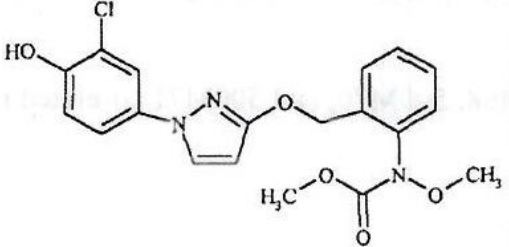
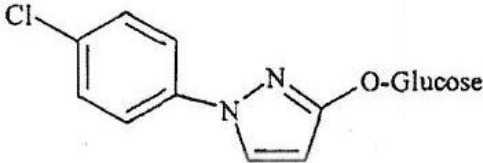
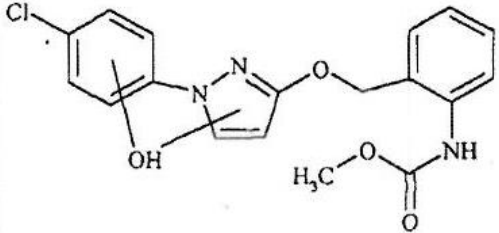
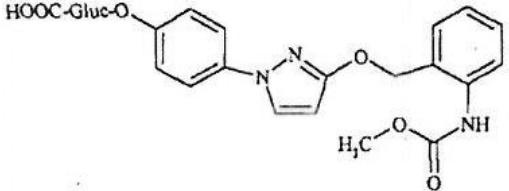
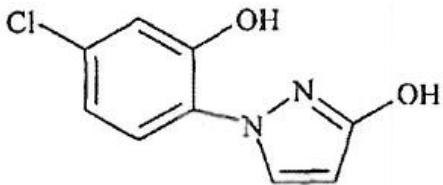
Common name/code Chemical name	Chemical structure	Matrices
Pyraclostrobin; BAS 500 F [Carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl] phenyl]methoxy-, methyl ester]		Grapes Potato foliage and tubers Wheat forage, grain, and straw Rotational Crops: 30-PBI radish roots and tops, and wheat forage and straw; 120-PBI wheat forage and straw; and 365-PBI wheat straw ^a Goat milk, muscle, fat, liver, and kidney ^a Poultry eggs and fat
BF 500-5; 500M04 1-(4-Chlorophenyl)-1H-pyrazol-3-ol		Potato foliage and tubers ^b Wheat forage, straw, and grain ^c Poultry eggs, fat, and liver Goat milk, liver, and kidney
500M05		Goat milk, liver, and kidney
500M06		Poultry eggs and liver

BF 500-3; 500M07 Methyl-N-[[[1-(4-chlorophenyl)pyrazol-3-yl]oxy]o-tolyl carbamate		Grapes Potato foliage and tubers Wheat forage, grain, and straw Rotational Crops: 30-PBI radish roots and tops, and wheat forage and straw; 120-PBI wheat forage and straw; and 365-PBI wheat straw ^a Goat milk, muscle, fat, liver, and kidney ^a Poultry eggs and fat
500M08		Goat milk and liver
500M24		Wheat grain
500M32		Poultry liver
500M34		Wheat forage and straw

500M39		Goat liver Poultry eggs and liver
500M45		Goat milk and liver
500M49		Poultry eggs, fat, and liver
500M51		Goat kidney
500M54		Grapes Potato foliage and tubers Wheat forage and straw

M55		Grapes
M56		Grapes
500M64		Goat milk and kidney Poultry eggs, fat, and liver
500M66		Goat milk, liver, and kidney Poultry liver
500M67		Goat milk, liver, and kidney

500M68		Potato foliage and tubers ^b Wheat forage, straw, and grain ^{c, d}
500M70		Wheat forage, straw, and grain ^{c, d}
500M71		Wheat forage, straw, and grain ^{c, d}
500M72; Tryptophan		Potato tubers Wheat grain
500M76		Wheat forage, straw, and grain ^c

BF 500-16; 500M77 Methyl N-[2-((1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-yl)oxymethyl)phenyl] N-methoxy carbamate		Poultry eggs, fat, and liver
500M79		Potato foliage and tubers
500M80		Poultry liver
500M83		Poultry liver
BF 500-8; 500M85 1-(4-Chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol		Goat milk, liver, and kidney

- ^a Pyraclostrobin and metabolite 500M07 co-eluted in goat milk and kidney, and in the rotational crops radish roots and tops, and wheat forage and straw.
- ^b Metabolites 500M04 and 500M68 co-eluted in potato foliage and tubers.
- ^c Metabolites 500M04 and 500M76, and glucosides 500M68, 500M70, and 500M71 co-eluted in wheat grain.
- ^d Glucosides 500M68, 500M70, and 500M7 co-eluted in wheat forage and straw.

APPENDIX C: Determination of Tolerances for Pyraclostrobin in/on Dill Seed and Fresh Herbs

The Organization for Economic Cooperation and Development statistical procedure was used to calculate tolerances for fresh basil, dried basil, fresh chives, fresh dill (dill weed), and dill seeds. The average combined residue of pyraclostrobin and BF 500-3 from each trial (n = 4) was used as the calculator entry value after adjustment to the proposed 1X application rate (factor 0.38).

Compound	pyraclostrobin
Crop	dill seed
Region / Country	USA
GAP	2X0.40X0.38propor
Total number of data (n)	4
Percentage of censored data	0%
Number of non-censored data	4
Lowest residue	1.460
Highest residue	19.700
Median residue	7.540
Mean	9.060
Standard deviation (SD)	7.666
Correction factor for censoring (CF)	1.000
<u>Proposed MRL estimate</u>	
- Highest residue	19.700
- Mean + 4 SD	39.723
- CF x 3 Mean	27.180
Unrounded MRL	39.723
Rounded MRL	<u>40</u>
High uncertainty of MRL estimate due to small dataset.	
Residues (mg/kg)	
19.700	
8.130	
6.950	
1.460	

Compound	Pyracolo-strobin		Pyraclo-strobin		Pyraclo-strobin	
Crop	basil (fresh)		dill (fresh, weed)		chives (fresh)	
Region / Country	USA		USA		USA	
GAP	2X0.40X0.38propor		2X0.40X0.38propor		2X0.40X0.38propor	
Total number of data (n)	4		4		4	
Percentage of censored data	0%		0%		0%	
Number of non-censored data	4		4		4	
Lowest residue	2.990		1.870		0.344	
Highest residue	6.110		7.220		2.980	
Median residue	3.695		3.405		2.735	
Mean	4.123		3.975		2.199	
Standard deviation (SD)	1.427		2.332		1.245	
Correction factor for censoring (CF)	1.000		1.000		1.000	
Proposed MRL estimate						
- Highest residue	6.110		7.220		2.980	
- Mean + 4 SD	9.830		13.304		7.180	
- CF x 3 Mean	12.368		11.925		6.596	
Unrounded MRL	12.368		13.304		7.180	
Rounded MRL	15		15		8	
	High uncertainty of MRL estimate due to small dataset.		High uncertainty of MRL estimate due to small dataset.		High uncertainty of MRL estimate due to small dataset.	
	Residues (mg/kg)		Residues (mg/kg)		Residues (mg/kg)	
	2.990		7.220		2.620	
	4.200		2.810		2.980	
	6.110		4.000		2.850	
	3.190		1.870		0.344	



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5

Crop Field Trial – Fresh Basil; Processed Food and Feed – Dried Basil

Primary Evaluator	Gary Otakie, Chemist HED/RRB4 (7509P)	Date: 10/25/07
Approved by	Susan V. Hummel, Branch Senior Scientist HED/RRB4 (7509P)	Date: 10/31/07

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713; submitted 7/31/2007). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

47014803. Carpenter, D.H. (2006) BAS 516: Magnitude of the Residue on Basil. Lab Project Number: 08792.03-BAR04. Unpublished study prepared by IR-4. 203 pages.

EXECUTIVE SUMMARY:

IR-4 has submitted field trial data for pyraclostrobin on basil. Four field trials were conducted in NAFTA Growing Zones 1 (NY, 1 trial), 3 (FL, 1 trial), 10 (CA, 1 trial), and 11 (WA, 1 trial) during the 2003 growing season. The test formulation used in all trials was BAS 500 02F, which was identified as either Headline® Fungicide (EPA Reg. No. 7969-186, 2.0 lb/gal EC) or Cabrio® Fungicide (EPA Reg. No. 7969-187, 20% WDG). BAS 500 02F was applied to basil as four directed foliar sprays at 0.20-0.21 lb ai/A/application for a total seasonal rate of 0.80-0.83 lb ai/A. Applications were made beginning when basil plants were at the vegetative/flowering stage and repeated on a 6- to 8-day retreatment interval using ground equipment (28-54 gal/A of spray volume) and did not include the use of a spray adjuvant. Applications included a tank mixture with another active ingredient (boscalid, formulated as BAS 510 UCF); only the residue data from treatments with pyraclostrobin are reported in this Data Evaluation Record.

Single control and duplicate treated samples of fresh basil were harvested from each test site at 0 and 3 days after treatment (DAT). Additional fresh basil samples were collected at 0 DAT and then dried according to simulated commercial practices in order to generate residue data for dried basil. Samples were stored frozen for up to 172 days prior to analysis, an interval supported by available storage stability data.

Samples of fresh and dried basil were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9908 entitled "Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS". Method D9908 is adequate for data collection based on acceptable concurrent method recoveries. The LOD and LOQ for fresh basil were statistically calculated as 0.008 ppm and 0.024 ppm for pyraclostrobin, and as 0.003 ppm and 0.010 ppm, respectively, for BF 500-3.



The results show that following four spray applications of pyraclostrobin (BAS 500 02F) totaling 0.80-0.83 lb ai/A, combined residues were 7.2-21.1 ppm in/on 8 samples of fresh basil harvested at 0 DAT, 1.3-7.5 ppm in/on 8 samples of fresh basil harvested at 3-4 DAT, and 40.1-80.6 ppm in/on dried basil harvested at 0 DAT. Average combined residues were 10.9 ppm in fresh basil harvested at 0 DAT, 4.8 ppm in fresh basil harvested at 3-4 DAT, and 67.5 ppm in dried basil harvested at 0 DAT. The processing of fresh basil to dried basil resulted in an increase of total residues with a processing factor range of 4.6-9.0x (average factor of 6.5x).

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the basil field trial data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 421145.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination and inhibits mycelial growth and sporulation of the fungus on the leaf surface. The fungicide is currently registered to BASF Corporation (BASF) for use on a variety of field, vegetable, fruit and nut crops. Permanent tolerances are established [40 CFR §180.582(a)(1)] for the combined residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3), expressed as parent, in/on numerous plant commodities at levels ranging from 0.02 ppm in/on wheat grain to 29 ppm in/on leafy vegetables, except *Brassica*. IR-4 has submitted field trial data in support label amendment for Pristine® Fungicide (EPA Reg. No.7969-199) to incorporate new uses on avocado, black sapote, canistel, mamey sapote, mango, papaya, sapodilla, star apple, and fresh herbs. Pristine® Fungicide is a WDG formulation containing multiple active ingredients of pyraclostrobin (12.8%) and boscalid (25.2%). The chemical structure and nomenclature of pyraclostrobin are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5

Crop Field Trial – Fresh Basil; Processed Food and Feed – Dried Basil

TABLE A.1. Pyraclostrobin Nomenclature.	
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl <i>N</i> -{2-[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yloxymethyl]phenyl}(<i>N</i> -methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use product (EP)	12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199, which also contains 25.2% of boscalid)

TABLE A.2. Physicochemical Properties of Technical Grade Pyraclostrobin.		
Parameter	Value	References ¹
Melting point/range	63.7-65.2EC	D269848 & D274191
pH	Not reported	D269848 & D274191
Density	1.285 g/cm ³ at 20EC	D269848 & D274191
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)	D269848 & D274191
Solvent solubility	acetone (≥160 mg/L); methanol (11 mg/L); 2-propanol (3.1 mg/L); ethyl acetate (≥160 mg/L); acetonitrile (≥76 mg/L); dichloromethane (≥110 mg/L); toluene (≥100 mg/L); n-heptane (0.36 mg/L); 1-octanol (2.4 mg/L); olive oil (2.9 mg/L); DMF (≥62 mg/L).	D269848 & D274191
Vapor pressure	2.6 x 10 ⁻¹⁰ hPa at 20EC 6.4 x 10 ⁻¹⁰ hPa at 25°C	D269848 & D274191
Dissociation constant, pK _a	Does not dissociate in water.	D269848 & D274191
Octanol/water partition coefficient, Log(K _{OW}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5	D269848 & D274191
UV/visible absorption spectrum	λ _{max} = 275 nm	D269848

¹ Product Chemistry data were reviewed by the Registration Division (DP# 269848 and D274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5

Crop Field Trial – Fresh Basil; Processed Food and Feed – Dried Basil

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.				
Trial Identification (City, State/Province; Year)	Soil characteristics			
	Type	% OM	pH	CEC (meq/g)
Freesville, NY 2003	Silt Loam	6.35	6.75	Not reported
Citra, FL 2003	Coarse Sand	1.92-2.04	5.6	Not reported
Salina, CA 2003	Loamy Sand	1.4	7.4	7.9
Moxee, WA 2003	Sandy Loam	0.96	6.3	Not reported

Weather conditions were considered normal for each test site during the study period. Temperature and rainfall were within the historical averages. Irrigation was used to supplement precipitation as needed. There were no meteorological abnormalities that occurred during the conduct of the study. Information on maintenance pesticides and fertilizers was also provided for each site.

TABLE B.1.2. Study Use Pattern for Pyraclostrobin.							
Location (City, State/Province; Year) Trial ID	End-use Product	Application Information					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI ¹ (days)	Total Rate (lb ai/A)	
Freeville, NY 2003 NY17	BAS 500 02F	Four broadcast foliar applications during flowering	31-32	0.20-0.21	6-8	0.83	None
Citra, FL 2003 FL55	BAS 500 02F	Four broadcast foliar applications from bloom to vegetation	30-31	0.20-0.21	7	0.82	None
Salina, CA 2003 CA 125	BAS 500 02F	Four broadcast foliar applications during vegetation	46-54	0.20	6-8	0.80	None
Moxee, WA 2003 WA18	BAS 500 02F	Four broadcast foliar applications during bloom	28-29	0.20-0.21	6-7	0.82	None

¹ RTI = Retreatment Interval.



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5

Crop Field Trial – Fresh Basil; Processed Food and Feed – Dried Basil

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Basil		
	Submitted	Requested ¹	
		Canada	US
1	1		
2			
3	1		
4			
5			
6			
7			
8			
9			
10	1		
11	1		
12			
Total	4		3

¹ OPPTS 860.1500 requires three field trials but does not specify the required geographic locations of residue field trials for basil.

B.2. Sample Handling and Preparation

Single control and duplicate treated samples (<2 lbs) of fresh basil were collected from each trial plot at 0 and 3 DAT. Additional samples (<0.5 lb) were collected at 0 DAT and dried according to local commercial practice. All samples were stored frozen within 1.5 hours of collection and then shipped frozen 7-33 days after harvest via ACDS Freezer truck to the analytical laboratory, BASF Agro Research (RTP, NC). Samples were received frozen from the field and stored in a freezer (< -10 °C) prior to homogenization and analysis.

B.3. Analytical Methodology

Samples of fresh and dried basil were analyzed for residues of pyraclostrobin and the metabolite BF 500-3 using BASF Analytical Method D9908 entitled “Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS”. Briefly, residues were extracted by shaking with methanol:water:2 N HCl (70:25:5; v:v:v) and centrifuged. Residues were then partitioned with cyclohexane, concentrated to dryness, and re-dissolved in buffered methanol:water (80:20, v:v). The final chromatographic analysis of residues was determined by LC/MS/MS. Total residues of pyraclostrobin and BF 500-3 are expressed as pyraclostrobin equivalents. The LOD and LOQ for fresh basil were statistically calculated as 0.008 ppm and 0.024 ppm for pyraclostrobin, and as 0.003 ppm and 0.010 ppm, respectively, for BF 500-3.

C. RESULTS AND DISCUSSION

In a total of four field trials conducted during 2003, pyraclostrobin was applied to basil as four broadcast foliar sprays at 0.20-0.21 lb ai/A/application through flowering and vegetation stages with RTIs of 6-8 days, for totals of 0.80-0.83 lb ai/A. All applications were made using ground equipment at 28-54 gal/A, and did not include the use of a spray adjuvant. Single control and duplicate treated samples of fresh basil were harvested from each test at 0 and 3 DAT.



Additional samples were harvested at 0 DAT and then dried according to simulated commercial practices.

Basil samples were stored frozen for 172 days prior to analysis. Storage stability data are available indicating that both pyraclostrobin and BF 500-3 are stable in frozen storage for 19-25 months in representative plant matrices (DP# 269668, L. Cheung, 11/28/01).

The LC/MS/MS method (BASF Method D9908) for determining residues of pyraclostrobin and BF 500-3 in/on basil was adequately validated in conjunction with the field trial. Concurrent recoveries of pyraclostrobin averaged 92% with a standard deviation of 15% in fresh basil and 85% with a standard deviation of 9% in dried basil. Average recovery of BF 500-3 in fresh basil was 94% with a standard deviation of 7% and in dried basil, average recovery was 83% with a standard deviation of 7% (see Table C.1). Apparent residues were <LOQ ppm in/on all control samples. Adequate sample calculations and example chromatograms were provided. Concurrent recoveries bracketed residues found in treated samples.

The results show that following four applications of pyraclostrobin totaling 0.80-0.83 lb ai/A, the combined residues were 7.2-21.1 ppm in/on 8 samples of fresh basil harvested at 0 DAT, 1.3-7.5 ppm in/on 8 samples of fresh basil harvested at 3-4 DAT, and 40.1-80.6 ppm in dried basil harvested at 0 DAT. The average processing factor for dried basil is 6.5x (see Table C.3). Average combined residues were 10.9 ppm in fresh basil harvested at 0 DAT, 4.8 ppm in fresh basil harvested at 3-4 DAT, and 67.5 ppm in dried basil harvested at 0 DAT (see Table C.4).

Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5

Crop Field Trial – Fresh Basil; Processed Food and Feed – Dried Basil

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin from Basil.				
Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean, \pm standard deviation (%)
Pyraclostrobin				
Fresh Basil	0.05	6	87, 103, 114, 104, 106, 119	106 \pm 11
	5.0	6	84, 78, 76, 76, 73, 87	79 \pm 5
	50.0	2	98, 82	90 \pm 11
	Total	14	73-119	92\pm15
Dried Basil	0.05	2	85, 101	93 \pm 11
	50.0	2	80, 80	80
	200	2	76, 90	8310 \pm
	Total	6	76-101	85\pm9
BF 500-3				
Fresh Basil	0.05	6	94, 87, 96, 84, 85, 88	89 \pm 5
	5.0	6	86, 83, 74, 75, 74, 89	80 \pm 7
	50.0	2	88, 77	83 \pm 8
	Total	14	74-94	84\pm7
Dried Basil	0.05	2	80, 94	87 \pm 10
	50.0	2	85, 78	82 \pm 5
	200	2	74, 85	80 \pm 8
	Total	6	74-94	83\pm7

TABLE C.2. Summary of Storage Conditions.			
Matrix	Storage Temperature (°C)	Actual Storage Duration, Days (days)	Interval of Demonstrated Storage Stability (months)
Fresh Basil	<-10	172	19-25 ¹
Dried Basil		161	

¹ DP# 269668, L. Cheung, 11/28/01.

TABLE C.3. Residue Data from Basil Field Trials with Pyraclostrobin.								
Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Commodity	PHI (days)	Residues (ppm)		
						Pyraclostrobin	BF 500-3	Combined
Freeville, NY 2003 NY17	1	Italian Large Leaf	0.83	Fresh Basil	0	8.42, 7.12	0.095, 0.087	8.52, 7.21
					3	3.93, 3.91	0.116, 0.124	4.05, 4.03
				Dried Basil	0	39.72	0.385	40.10 [5.1x] ¹
Citra, FL 2003 FL55	3	Degenova	0.82	Fresh Basil	0	8.98, 12.7	0.179, 0.271	9.16, 12.97
					4	7.11, 5.44	0.303, 0.252	7.41, 5.69
				Dried Basil	0	78.8	1.77	80.57 [7.3x] ¹
Salina, CA 2003 CA 125	10	Genovese	0.80	Fresh Basil	0	20.8, 10.9	0.279, 0.190	21.07, 11.09
					4	1.23, 1.20	0.065, 0.071	1.30, 1.27
				Dried Basil	0	72.68	1.069	73.75 [4.6x] ¹
Moxee, WA 2003 WA18	11	Italian Large Leaf	0.82	Fresh Basil	0	7.94, 8.54	0.136, 0.157	8.08, 8.70
					3	7.02, 7.23	0.284, 0.269	7.30, 7.50
				Dried Basil	0	74.4	1.339	75.74 [9.0x] ¹

¹ Values in bracket are the processing factors calculated from drying of fresh basil. The average residues of two fresh basil samples were used for calculation.



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5

Crop Field Trial – Fresh Basil; Processed Food and Feed – Dried Basil

TABLE C.4. Summary of Combined Residue Data from Basil Field Trials with Pyraclostrobin.									
Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT	Median (STMdR)	Mean (STMR)	Std. Dev.
Fresh Basil	0.80-0.83	0	8	7.2	21.1	16.1	8.9	10.9	4.5
		3-4	8	1.3	7.5	7.4	4.9	4.8	2.6
Dried Basil		0	4	40.1	80.6	80.6	74.7	67.5	18.5

D. CONCLUSION

The field trial data are adequate and support the use of pyraclostrobin on basil for four broadcast foliar sprays at ~0.20 lb ai/A/application during crop development, for a total seasonal rate of ~0.80 lb ai/A. The data support a minimum RTI of 6 days, a 0- or 3-day PHI for fresh basil and a 0-day PHI for dried basil. The average processing factor for dried basil is 6.5x.

E. REFERENCES

DP#s: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429
Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

F. DOCUMENT TRACKING

RDI: G. Otakie 10/25/07; S. Hummel 10/31/07
Petition Number: 6E7165
DP#: 421145
PC Code: 099100

Template Version June 2005



Primary Evaluator	Gary Otakie, Chemist HED/RRB4 (7509P)	Date: 10/25/07
Approved by	Susan V. Hummel, Branch Senior Scientist HED/RRB4 (7509P)	Date: 10/31/07

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713; submitted 7/31/2007). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

47014802. Carpenter, D.H. (2006) BAS 516: Magnitude of the Residue on Chives. Lab Project Number: 08793.03-BAR50. Unpublished study prepared by IR-4. 173 pages.

EXECUTIVE SUMMARY:

IR-4 has submitted field trial data for pyraclostrobin on chives. Four field trials were conducted in NAFTA Growing Zones 2 (MD, 1 trial), 5 (OH, 1 trial), 10 (CA, 1 trial), and 11 (WA, 1 trial) during the 2003 growing season. The test formulation used in all trials was BAS 500 02F, which was identified as either Headline® Fungicide (EPA Reg. No. 7969-186, 2.0 lb/gal EC) or Cabrio® Fungicide (EPA Reg. No. 7969-187, 20% WDG). BAS 500 02F was applied to chives as four directed foliar sprays at 0.20-0.21 lb ai/A/application for a total seasonal rate of 0.80-0.83 lb ai/A. Applications were made beginning when chive plants were at the vegetative stage and repeated on a 6- to 8-day retreatment interval using ground equipment (24-50 gal/A of spray volume) and did not include the use of a spray adjuvant. Applications included a tank mixture with another active ingredient (boscalid, formulated as BAS 510 UCF); only the residue data from treatments with pyraclostrobin are reported in this Data Evaluation Record.

Single control and duplicate treated samples of fresh chives were harvested immediately from each trial site following the last treatment (0 DAT). Samples were stored frozen for up to 115 days prior to analysis, an interval supported by available storage stability data.

Samples of harvested chives were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9908 entitled "Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS". Method D9908 is adequate for data collection based on acceptable concurrent method recoveries. The LOQ and LOD for fresh chives were statistically calculated as 0.029 ppm and 0.01 ppm for pyraclostrobin, and as 0.02 ppm and 0.007 ppm, respectively, for BF 500-3.



The results show that following four applications of pyraclostrobin (BAS 500 02F) totaling 0.81-0.83 lb ai/A, combined residues were 0.7-8.8 ppm in/on 8 samples of fresh chives harvested immediately following the last treatment (0 DAT). The average combined residues in/on treated samples were 5.8 ppm.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the chive field trial data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 421145.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination and inhibits mycelial growth and sporulation of the fungus on the leaf surface. The fungicide is currently registered to BASF Corporation (BASF) for use on a variety of field, vegetable, fruit and nut crops. Permanent tolerances are established [40 CFR §180.582(a)(1)] for the combined residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3), expressed as parent, in/on numerous plant commodities at levels ranging from 0.02 ppm in/on wheat grain to 29 ppm in/on leafy vegetables, except *Brassica*. IR-4 has submitted field trial data in support label amendment for Pristine® Fungicide (EPA Reg. No.7969-199) to incorporate new uses on avocado, black sapote, canistel, mamey sapote, mango, papaya, sapodilla, star apple, and fresh herbs. Pristine® Fungicide is a WDG formulation containing multiple active ingredients of pyraclostrobin (12.8%) and boscalid (25.2%). The chemical structure and nomenclature of pyraclostrobin are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.


TABLE A.1. Pyraclostrobin Nomenclature.

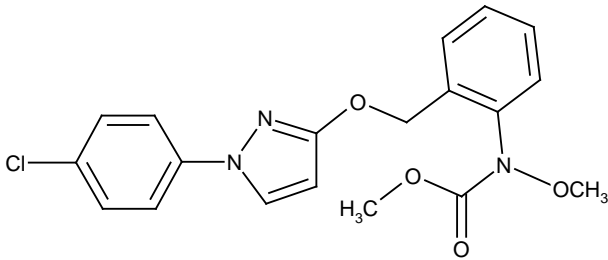
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl <i>N</i> -[2-[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxymethyl]phenyl] (<i>N</i> -methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use product (EP)	12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199, which also contains 25.2% of boscalid)

TABLE A.2. Physicochemical Properties of Technical Grade Pyraclostrobin.

Parameter	Value	References ¹																									
		Laboratory Project Number	MRID																								
Melting point/range	63.7-65.2 °C	PCP03796: 1996/10327	45118213																								
pH	Not reported																										
Density	1.285 g/cm ³ at 20°C	PCF01847: 1998/10768	45118212																								
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)	PCP03797: 1996/10939 PCP04015: 1997/10693	45118233 45118234																								
Solvent solubility	<table><thead><tr><th>Solvent</th><th>Solubility (mg/L)</th></tr></thead><tbody><tr><td>acetone</td><td>≥ 160</td></tr><tr><td>methanol</td><td>11</td></tr><tr><td>2-propanol</td><td>3.1</td></tr><tr><td>ethyl acetate</td><td>≥ 160</td></tr><tr><td>acetonitrile</td><td>≥ 76</td></tr><tr><td>dichloromethane</td><td>≥ 110</td></tr><tr><td>toluene</td><td>≥ 100</td></tr><tr><td>n-heptane</td><td>0.36</td></tr><tr><td>1-octanol</td><td>2.4</td></tr><tr><td>olive oil</td><td>2.9</td></tr><tr><td>DMF</td><td>≥ 62</td></tr></tbody></table>	Solvent	Solubility (mg/L)	acetone	≥ 160	methanol	11	2-propanol	3.1	ethyl acetate	≥ 160	acetonitrile	≥ 76	dichloromethane	≥ 110	toluene	≥ 100	n-heptane	0.36	1-octanol	2.4	olive oil	2.9	DMF	≥ 62	PCP04037: 1996/10954	45118228
Solvent	Solubility (mg/L)																										
acetone	≥ 160																										
methanol	11																										
2-propanol	3.1																										
ethyl acetate	≥ 160																										
acetonitrile	≥ 76																										
dichloromethane	≥ 110																										
toluene	≥ 100																										
n-heptane	0.36																										
1-octanol	2.4																										
olive oil	2.9																										
DMF	≥ 62																										
Vapor pressure	2.6 x 10 ⁻¹⁰ hPa at 20°C 6.4 x 10 ⁻¹⁰ hPa at 25°C	PCF01721: 1997/10646	45118214																								
Dissociation constant, pK _a	Does not dissociate in water.																										
Octanol/water partition coefficient, Log(K _{OW}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5	PCP03883: 1996/10383	45118215																								
UV/visible absorption spectrum	λ _{max} = 275 nm	PCP03799: 1996/10955	47220801																								

¹ Product Chemistry data were reviewed by the Registration Division under DP Barcode Numbers D269848 and D274191 (memo from S. Malak dated 03/May/2001; 20 pages).



B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.				
Trial Identification (City, State/Province; Year)	Soil characteristics			
	Type	% OM	pH	CEC (meq/g)
Salisbury, MD 2003	Loamy Sand	1.1	6.6	2.59
Willard, OH 2003	Sandy Loam	41.87	6.3	Not reported
Salinas, CA 2003	Loamy Sand	1.4	7.4	7.9
Moxee WA 2003	Sandy Loam	0.96	6.3	Not reported

Weather conditions were considered normal for each test site during the study period. Temperature and rainfall were within the historical averages. Irrigation was used to supplement precipitation as needed. There were no meteorological abnormalities that occurred during the conduct of the study. Information on maintenance pesticides and fertilizers was also provided for each site.

TABLE B.1.2. Study Use Pattern for Pyraclostrobin.							
Location (City, State/Province; Year) Trial ID	End-use Product	Application Information					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI ¹ (days)	Total Rate (lb ai/A)	
Salisbury, MD 2003	BAS 500 02F	Four broadcast foliar applications to mature leaves	24	0.20	6-8	0.81	None
Willard, OH 2003	BAS 500 02F	Four broadcast foliar applications during vegetation	27, 29	0.20-0.21	6-8	0.83	None
Salinas, CA 2003	BAS 500 02F	Four broadcast foliar applications during vegetation	50, 53	0.20-0.21	6-7	0.81	None
Moxee WA 2003	BAS 500 02F	Four broadcast foliar applications during vegetation	29, 28	0.20-0.21	7-8	0.82	None

¹ RTI = Retreatment Interval.

**TABLE B.1.3. Trial Numbers and Geographical Locations.**

NAFTA Growing Zones	Chives		
	Submitted	Requested ¹	
		Canada	US
1			
2	1		
3			
4			
5	1		
6			
7			
8			
9			
10	1		
11	1		
12			
Total	4		3

¹ OPPTS 860.1500 requires three field trials but does not specify the geographic locations of the required residue field trials for chives.

B.2. Sample Handling and Preparation

Single control and duplicate treated samples (<2 lb) of mature chives were collected from each trial plot at 0 DAT. Fresh samples were stored frozen within 2.5 hours of collection and shipped frozen 10-60 days after harvest via ACDS Freezer truck to the analytical laboratory, BASF Agro Research (RTP, NC). Samples were received frozen from the field and were stored in a freezer (< -10 °C) prior to homogenization and analysis.

B.3. Analytical Methodology

Samples of fresh chives were analyzed for residues of pyraclostrobin and the metabolite BF 500-3 using BASF Analytical Method D9908 entitled “Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS”. Briefly, residues were extracted by shaking with methanol:water:2 N HCl (70:25:5; v:v:v) and centrifuged. Residues were then partitioned with cyclohexane, concentrated to dryness, and re-dissolved in buffered methanol:water (80:20, v:v). The final chromatographic analysis of residues was determined by LC/MS/MS. Total residues of pyraclostrobin and BF 500-3 are expressed as pyraclostrobin equivalents. The LOQ and LOD for fresh chives were statistically calculated as 0.029 ppm and 0.01 ppm for pyraclostrobin, and as 0.02 ppm and 0.007 ppm, respectively, for BF 500-3.

The adequacy of Method D9908 was verified by fortifying control samples of chives with pyraclostrobin and BF 500-3 at 0.05 to 40.0 ppm.



C. RESULTS AND DISCUSSION

In a total of four field trials conducted during 2003, pyraclostrobin (BAS 500 02F) was applied to chives as four broadcast foliar sprays at 0.20-0.21 lb ai/A/application through vegetative development at RTIs of 6-8 days, for totals of 0.81-0.83 lb ai/A. All applications were made using ground equipment at 24-50 gal/A, and did not include the use of a spray adjuvant. Single control and duplicate treated samples of chives were harvested from each test at 0 DAT.

Chive samples were stored frozen for 115 days prior to analysis. Storage stability data are available indicating that both pyraclostrobin and BF 500-3 are stable in frozen storage for 19-25 months in representative plant matrices (DP# 269668, L. Cheung, 11/28/01).

The LC/MS/MS method (BASF Method D9908) for determining residues of pyraclostrobin and BF 500-3 in/on chives was adequately validated in conjunction with the field trials. Concurrent recoveries of pyraclostrobin averaged 86% with a standard deviation of 12%, and recovery of BF 500-3 averaged 81% with a standard deviation of 8% (see Table C.1). Apparent residues of pyraclostrobin were <LOQ ppm in/on all control samples. Adequate sample calculations and example chromatograms were provided. Concurrent recoveries bracketed residues found in treated samples.

The results indicate that following four applications of pyraclostrobin (BAS 500 02F) totaling 0.81-0.83 lb ai/A, the combined residues were 0.7-8.8 ppm in/on 8 samples of chives harvested at 0 DAT (see Table C.3). Average combined residues were 5.8 ppm, and the HAFT was 7.8 ppm (see Table C.4).

Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin from Chives.				
Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean, \pm standard deviation (%)
Pyraclostrobin				
Chives	0.02	5	95, 91, 44 ¹ , 80, 115, 90	94 \pm 13
	5.0	4	82, 80, 74, 77	78 \pm 4
	50.0	2	85, 76	81 \pm 6
	Total	11	74-115	86 \pm 12
BF 500-3				
Chives	0.02	6	99, 88, 82, 77, 88, 75	85 \pm 9
	5.0	4	77, 75, 72, 78	76 \pm 3
	50.0	2	87, 74	81 \pm 9
	Total	12	72-99	81 \pm 8

**TABLE C.2. Summary of Storage Conditions.**

Matrix	Storage Temperature (°C)	Actual Storage Duration, Days (days)	Interval of Demonstrated Storage Stability (months)
Chives	<-10	115	19-25 ¹

¹ DP# 269668, L. Cheung, 11/28/01.**TABLE C.3. Residue Data from Chive Field Trials with Pyraclostrobin.**

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Commodity	PHI (days)	Residues (ppm)		
						Pyraclostrobin	BF 500-3	Combined
Salisbury, MD 2003	2	Staro	0.81	Chives	0	6.6, 6.7	0.25, 0.26	6.85, 6.96
Willard, OH 2003	5	Fancy	0.83	Chives	0	8.7, 6.8	0.09, 0.07	8.79, 6.87
Salinas, CA 2003	10	Purly	0.81	Chives	0	7.8, 6.9	0.17, 0.15	7.97, 7.05
Moxee WA 2003	11	Staro	0.82	Chives	0	0.69, 1.1	0.03, 0.04	0.71, 1.10

TABLE C.4. Summary of Combined Residue Data from Chive Field Trials with Pyraclostrobin.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT	Median (STMdR)	Mean (STMR)	Std. Dev.
Chives	0.81-0.83	0	8	0.7	8.8	7.8	6.9	5.8	3.1

D. CONCLUSION

The chive field trial data are adequate and support the use of pyraclostrobin (BAS 500 02F) as four broadcast foliar sprays at ~0.20 lb ai/A/application during crop development for a total seasonal rate of ~0.80 lb ai/A. The data support a minimum RTI of 6 days and a 0-day PHI.

E. REFERENCES

DP#s: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429
Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901



Pyraclostrobin/BAS 500 F/PC Code 099100/IR-4

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3

Crop Field Trial - Chives

F. DOCUMENT TRACKING

RDI: G. Otakie 10/25/07; S. Hummel 10/31/07

Petition Number: 6E7165

DP#: 421145

PC Code: 099100

Template Version June 2005



Primary Evaluator	Gary Otakie, Chemist HED/RRB4 (7509P)	Date: 10/25/07
Approved by	Susan V. Hummel, Branch Senior Scientist HED/RRB4 (7509P)	Date: 10/31/07

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713; submitted 7/31/2007). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

47014801. Carpenter, D.H. (2006) BAS 516: Magnitude of the Residue on Dill. Lab Project Number: 08691. Unpublished study prepared by BASF Corporation. 214 pages.

EXECUTIVE SUMMARY:

IR-4 has submitted field trial data for pyraclostrobin on dill. Four field trials were conducted in NAFTA Growing Zones 2 (MD, 1 trial), 3 (FL, 1 trial), 10 (CA, 1 trial), and 11 (WA, 1 trial) during the 2003 growing season. The test formulation used in all trials was BAS 500 02F, which was identified as either Headline® Fungicide (EPA Reg. No. 7969-186, 2.0 lb/gal EC) or Cabrio® Fungicide (EPA Reg. No. 7969-187, 20% WDG). BAS 500 02F was applied to dill as four directed foliar sprays at 0.19-0.21 lb ai/A/application for a total seasonal rate of 0.80-0.83 lb ai/A. Applications were made beginning when dill plants were at the vegetative growth stage through seed production; the retreatment intervals were 6 to 8 days. Foliar sprays were made using ground equipment (28-62 gal/A of spray volume) and did not include the use of a spray adjuvant. Applications included a tank mixture with another active ingredient (boscalid, formulated as BAS 510 UCF); only the residue data from treatments with pyraclostrobin are reported in this Data Evaluation Record.

Single control and duplicate treated samples of fresh dill and dill seeds were harvested immediately from each trial site following the last treatment (0 DAT). Samples were stored frozen for up to 171 days prior to analysis, an interval supported by available storage stability data.

Samples of harvested fresh dill and dill seeds were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9908 entitled "Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS". Method D9908 is adequate for data collection based on acceptable concurrent method recoveries. The LOQ and LOD for fresh dill were statistically calculated as 0.023 ppm and 0.008 ppm for pyraclostrobin, and as 0.030 ppm and 0.010 ppm, respectively, for BF 500-3.



The results show that following four applications of pyraclostrobin (BAS 500 02F) totaling 0.80-0.83 lb ai/A, combined residues at 0 DAT ranged 3.98-19.54 ppm in/on 8 samples of fresh dill and 3.60-22.60 ppm in/on 6 samples of dill seed. The average combined residues were 10.46 ppm in/on treated fresh dill and 14.45 ppm in/on treated dill seed.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the dill field trial data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 421145.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination and inhibits mycelial growth and sporulation of the fungus on the leaf surface. The fungicide is currently registered to BASF Corporation (BASF) for use on a variety of field, vegetable, fruit and nut crops. Permanent tolerances are established [40 CFR §180.582(a)(1)] for the combined residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3), expressed as parent, in/on numerous plant commodities at levels ranging from 0.02 ppm in/on wheat grain to 29 ppm in/on leafy vegetables, except *Brassica*. IR-4 has submitted field trial data in support label amendment for Pristine® Fungicide (EPA Reg. No.7969-199) to incorporate new uses on avocado, black sapote, canistel, mamey sapote, mango, papaya, sapodilla, star apple, and fresh herbs. Pristine® Fungicide is a WDG formulation containing multiple active ingredients of pyraclostrobin (12.8%) and boscalid (25.2%). The chemical structure and nomenclature of pyraclostrobin are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.



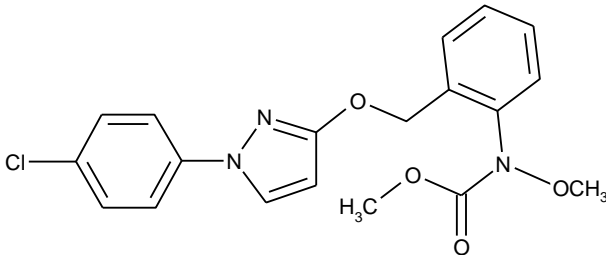
TABLE A.1. Pyraclostrobin Nomenclature.	
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl <i>N</i> -{2-[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yloxymethyl]phenyl}(<i>N</i> -methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use product (EP)	12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199, which also contains 25.2% of boscalid)

TABLE A.2. Physicochemical Properties of Technical Grade Pyraclostrobin.																											
Parameter	Value	References ¹																									
		Laboratory Project Number	MRID																								
Melting point/range	63.7-65.2 °C	PCP03796: 1996/10327	45118213																								
pH	Not reported																										
Density	1.285 g/cm ³ at 20°C	PCF01847: 1998/10768	45118212																								
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)	PCP03797: 1996/10939 PCP04015: 1997/10693	45118233 45118234																								
Solvent solubility	<table><tr><td><u>Solvent</u></td><td><u>Solubility (mg/L)</u></td></tr><tr><td>acetone</td><td>≥ 160</td></tr><tr><td>methanol</td><td>11</td></tr><tr><td>2-propanol</td><td>3.1</td></tr><tr><td>ethyl acetate</td><td>≥ 160</td></tr><tr><td>acetonitrile</td><td>≥ 76</td></tr><tr><td>dichloromethane</td><td>≥ 110</td></tr><tr><td>toluene</td><td>≥ 100</td></tr><tr><td>n-heptane</td><td>0.36</td></tr><tr><td>1-octanol</td><td>2.4</td></tr><tr><td>olive oil</td><td>2.9</td></tr><tr><td>DMF</td><td>≥ 62</td></tr></table>	<u>Solvent</u>	<u>Solubility (mg/L)</u>	acetone	≥ 160	methanol	11	2-propanol	3.1	ethyl acetate	≥ 160	acetonitrile	≥ 76	dichloromethane	≥ 110	toluene	≥ 100	n-heptane	0.36	1-octanol	2.4	olive oil	2.9	DMF	≥ 62	PCP04037: 1996/10954	45118228
<u>Solvent</u>	<u>Solubility (mg/L)</u>																										
acetone	≥ 160																										
methanol	11																										
2-propanol	3.1																										
ethyl acetate	≥ 160																										
acetonitrile	≥ 76																										
dichloromethane	≥ 110																										
toluene	≥ 100																										
n-heptane	0.36																										
1-octanol	2.4																										
olive oil	2.9																										
DMF	≥ 62																										
Vapor pressure	2.6 x 10 ⁻¹⁰ hPa at 20°C 6.4 x 10 ⁻¹⁰ hPa at 25°C	PCF01721: 1997/10646	45118214																								
Dissociation constant, pK _a	Does not dissociate in water.																										
Octanol/water partition coefficient, Log(K _{ow}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5	PCP03883: 1996/10383	45118215																								
UV/visible absorption spectrum	λ _{max} = 275 nm	PCP03799: 1996/10955	47220801																								

¹ Product Chemistry data were reviewed by the Registration Division under DP Barcode Numbers D269848 and D274191 (memo from S. Malak dated 03/May/2001; 20 pages).



B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.				
Trial Identification (City, State/Province; Year)	Soil characteristics			
	Type	%OM	pH	CEC (meq/g)
Citra, FL 2003	Coarse Sand	1.92-2.04	5.6	Not reported
Salinas, CA 2003	Sandy Loam	2.0	7.2	14
Moxee, CA 2003	Sandy Loam	0.99	6.7	Not reported
Salisbury, MD 2003	Loamy Sand	0.8-0.9	5.8-6.1	Not reported

Weather conditions were considered normal for each test site during the study period. Temperature and rainfall were within the historical averages. Irrigation was used to supplement precipitation as needed. There were no meteorological abnormalities that occurred during the conduct of the study. Information on maintenance pesticides and fertilizers was also provided for each site.

TABLE B.1.2. Study Use Pattern for Pyraclostrobin.							
Location (City, State/Province; Year) Trial ID	End-use Product	Application Information					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI ¹ (days)	Total Rate (lb ai/A)	
Citra, FL 2003 FL54	BAS 500 02F	Four broadcast foliar applications during vegetation	30, 31	0.20	7	0.81	None
		Five broadcast foliar applications during seed development	30	0.20	7-8	1.0	None
Salinas, CA 2003 CA124	BAS 500 02F	Four broadcast foliar applications during vegetation	47, 62	0.20-0.21	6-7	0.82	None
		Four broadcast foliar applications during seed development	42, 43	0.19-0.20	6-7	0.80	None
Moxee, CA 2003 WA17	BAS 500 02F	Four broadcast foliar applications during vegetation	29, 28	0.20-0.21	6-7	0.82	None
		Four broadcast foliar applications during seed development	28, 29	0.20-0.21	7-8	0.83	None
Salisbury, MD 2003 MD23	BAS 500 02F	Four broadcast foliar applications during vegetation	26	0.20	6-8	0.81	None

¹ RTI = Retreatment interval.

**TABLE B.1.3. Trial Numbers and Geographical Locations.**

NAFTA Growing Zones	Dill		
	Submitted	Requested ¹	
		Canada	US
1			
2	1		
3	1		
4			
5			
6			
7			
8			
9			
10	1		
11	1		
12			
Total	4		3

¹ OPPTS 860.1500 requires three trials with two treated samples at 1X or two trials with four treated samples (two at 1X and two at 2X per trial) but does not specify the geographic locations of the required trials for dill.

B.2. Sample Handling and Preparation

Single control and duplicate treated samples of fresh dill (<2 lbs) and of dried dill seed (<0.5 lb) were collected from each test plot at 0 DAT. Fresh samples were stored frozen within 45 minutes of collection, and seed samples were stored frozen within 80 minutes of collection. Samples were shipped frozen 26-56 days after harvest via ACDS Freezer truck to the analytical laboratory, BASF Agro Research (RTP, NC). Samples were received frozen from the field and were stored in a freezer (< -10 °C) prior to homogenization and analysis.

B.3. Analytical Methodology

Samples of fresh dill and dill seeds were analyzed for residues of pyraclostrobin and the metabolite BF 500-3 using BASF Analytical Method D9908 entitled “Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS”. Briefly, residues were extracted by shaking with methanol:water:2 N HCl (70:25:5; v:v:v) and centrifuged. Residues were then partitioned with cyclohexane, concentrated to dryness, and re-dissolved in buffered methanol:water (80:20, v:v). The final chromatographic analysis of residues was determined by LC/MS/MS. Total residues of pyraclostrobin and BF 500-3 are expressed as pyraclostrobin equivalents. The LOQ and LOD for fresh dill were statistically calculated as 0.023 ppm and 0.008 ppm for pyraclostrobin, and as 0.030 ppm and 0.010 ppm, respectively, for BF 500-3.

The adequacy of Method D9908 was verified by fortifying control samples of fresh dill with pyraclostrobin and BF 500-3 at 0.05 to 40.0 ppm; control samples of dill seed were fortified at 0.05 to 200 ppm.



C. RESULTS AND DISCUSSION

In a total of four field trials conducted during 2003, pyraclostrobin was applied to dill as four directed foliar applications at 0.19-0.21 lb ai/A/application from vegetative development stage through seed production with RTIs of 6-8 days, for totals of 0.80-0.83 lb ai/A. All applications were made using ground equipment at 28-62 gal/A, and did not include the use of a spray adjuvant. At the FL trial, a fifth application was made to the plot designated for seed harvest, as the crop was immature at the time of the fourth application. A total of 1.0 lb ai/A was applied to this FL plot. Single control and duplicate treated samples of fresh dill and dill seed were harvested from each trial site at 0 DAT.

The harvested samples of fresh dill and dill seed were stored frozen for 171 and 147 days, respectively, prior to analysis. Storage stability data are available indicating that both pyraclostrobin and BF 500-3 are stable in frozen storage for 19-25 months in representative plant matrices (DP# 269668, L. Cheung, 11/28/01).

The LC/MS/MS method (BASF Method D9908) for determining residues of pyraclostrobin and BF 500-3 in/on fresh dill and dill seed was adequately validated in conjunction with the field trial. Concurrent recoveries of pyraclostrobin on fresh dill averaged 89% with a standard deviation of 10%, and the average recovery from dill seed was 82% with a standard deviation of 9%. The average recovery of BF 500-3 from fresh dill was 90% with a standard deviation of 11%, and the average recovery from dill seed was 76% with a standard deviation of 9% (see Table C.1). Apparent residues of pyraclostrobin were <LOQ ppm in/on all control samples. Adequate sample calculations and example chromatograms were provided. Concurrent recoveries bracketed residues found in treated samples.

The results indicate that following four applications of pyraclostrobin (BAS 500 02F) totaling 0.80-0.83 lb ai/A, combined residues at 0 DAT ranged 3.98-19.54 ppm in/on 8 samples of fresh dill and 3.60-22.60 ppm in/on 6 samples of dill seed (see Table C.3). Average combined residues were 10.46 ppm in/on fresh dill and 14.45 ppm in/on dill seed. The HAFT was 19.01 ppm for fresh dill and 21.20 ppm for dill seed (see Table C.4). Combined residues from the FL trial that included a fifth application to dill seed were 49.2 and 54.4 ppm, an obvious outlier and not in the same population as the remaining samples; these values were not included in the statistical calculation.

Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.



TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin from Dill.				
Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean, \pm standard deviation (%)
Pyraclostrobin				
Fresh Dill	0.02	6	91, 79, 109, 94, 78, 84	89 \pm 12
	5.0	4	95, 86, 79, 80	85 \pm 7
	40.0	2	95, 98	97 \pm 2
	Total	12	78-109	89\pm10
Dill Seed	0.02	4	98, 86, 78, 90	88 \pm 8
	5.0	2	79, 80	80 \pm 1
	200	2	71, 76	74 \pm 4
	Total	8	71-98	82\pm9
BF 500-3				
Fresh Dill	0.02	6	85, 71, 115, 97, 98, 88	92 \pm 15
	5.0	4	94, 91, 80, 80	86 \pm 7
	40.0	2	93, 92	93 \pm 1
	Total	12	71-115	90\pm11
Dill Seed	0.02	4	67, 70, 87, 93	79 \pm 13
	5.0	2	72, 72	72
	200	2	71, 77	74 \pm 4
	Total	8	67-93	76\pm9

TABLE C.2. Summary of Storage Conditions.			
Matrix	Storage Temperature (°C)	Actual Storage Duration, Days (days)	Interval of Demonstrated Storage Stability (months)
Fresh Dill	<-10	171	19-25 ¹
Dill Seed		147	

¹ DP# 269668, L. Cheung, 11/28/01.

TABLE C.3. Residue Data from Dill Field Trials with Pyraclostrobin.								
Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Commodity	PHI (days)	Residues (ppm)		
						Pyraclostrobin	BF 500-3	Combined
Citra, FL 2003 FL54	3	Bouquet	0.81	Fresh Dill	0	18.96, 17.92	0.575, 0.562	19.54, 18.48
			1.0	Dill Seed	0	47.2, 52.6	2.03, 1.81	49.2, 54.4
Salinas, CA 2003 CA124	10	Bouquet	0.82	Fresh Dill	0	5.60, 8.85	0.141, 0.193	5.74, 9.04
			0.80	Dill Seed	0	19.2, 21.5	1.02, 1.05	20.2, 22.6
Moxee, CA 2003 WA17	11	Island Mammoth	0.82	Fresh Dill	0	9.99, 10.5	0.280, 0.30	10.27, 10.8
			0.83	Dill Seed	0	17.4, 17.9	0.613, 0.651	18.0, 18.6
Salisbury, MD 2003 MD23	2	Superdukat	0.81	Fresh Dill	0	3.84, 5.66	0.144, 0.190	3.98, 5.85
			0.81	Dill Seed	0	3.34, 3.84	0.251, 0.281	3.6, 4.1



TABLE C.4. Summary of Combined Residue Data from Dill Field Trials with Pyraclostrobin.									
Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT	Median (STMdR)	Mean (STMR)	Std. Dev.
Fresh Dill	0.81-0.82	0	8	3.98	19.54	19.01	9.66	10.46	5.79
Dill Seed	0.80-0.83	0	6	3.60	22.60	21.20	18.30	14.45	8.34

D. CONCLUSION

The dill field trial data are adequate and support the use of pyraclostrobin (BAS 500 02F) as four broadcast foliar sprays at ~0.20 lb ai/A/application during crop development for a total seasonal rate of ~0.80 lb ai/A. The data support a minimum RTI of 6 days and a 0-day PHI.

E. REFERENCES

DP#s: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429
Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

F. DOCUMENT TRACKING

RDI: G. Otakie 10/25/07; S. Hummel 10/31/07
Petition Number: 6E7165
DP#: 421145
PC Code: 099100

Template Version June 2005